

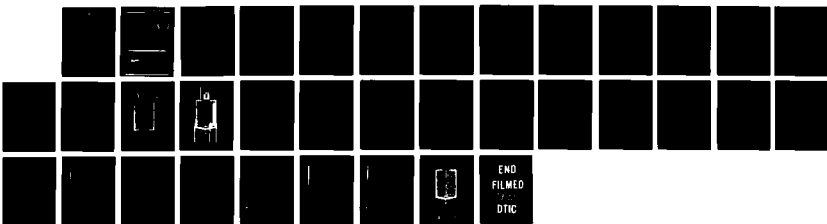
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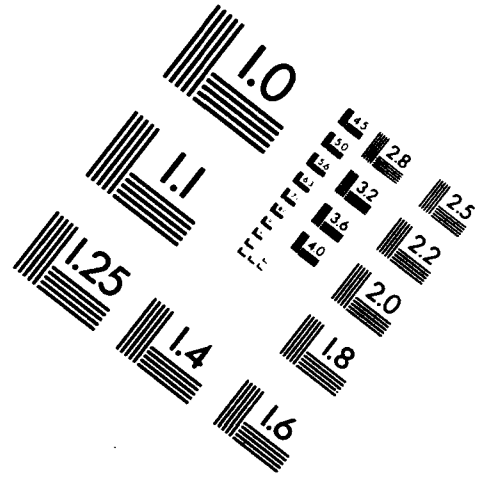
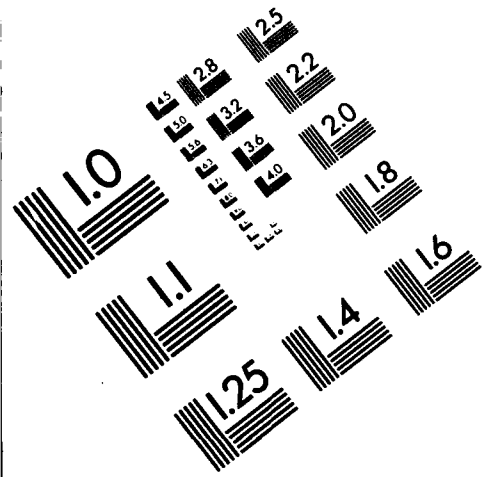




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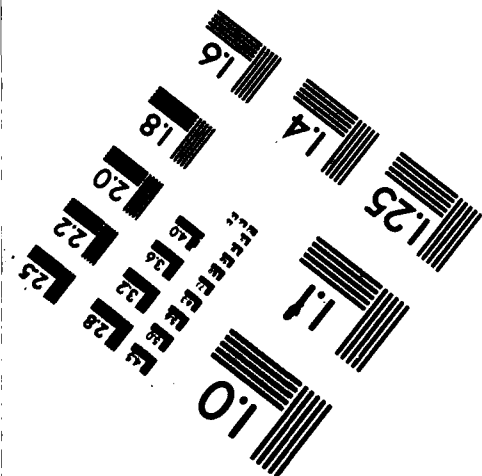
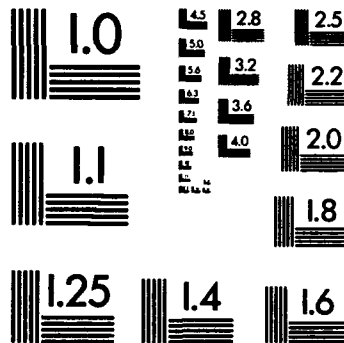
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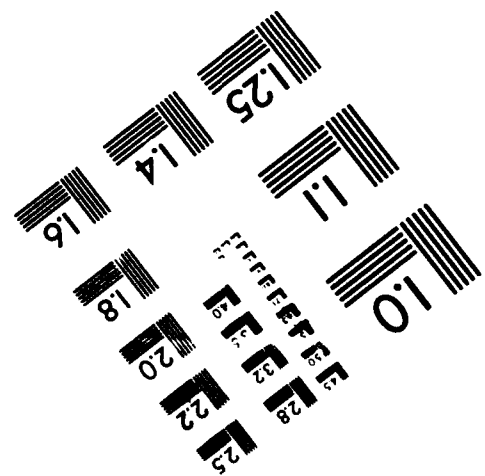
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**FREON RECOVERY FROM NITROGEN TETROXIDE AND
FREON SOLUTIONS**

Robert O. Bucsh

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Phillips Laboratory
OLAC-PL/RKFE
Edwards AFB California 93524-7680

April 1993

Final Report

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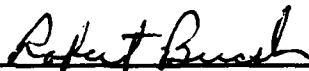
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FOREWORD

This final report was submitted by the OLAC PL/RKFE Branch, at the Phillips Laboratory, Edwards AFB CA 93524-7680. OLAC PL Project Manager was Robert O. Bucsh

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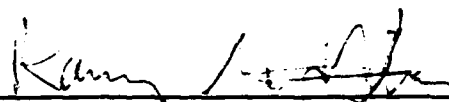
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13. ABSTRACT (MAXIMUM 200 WORDS) A reactor was designed, built, and tested to extract N ₂ O ₄ from a N ₂ O ₄ in Freon solution. A two step chemistry process was developed, the N ₂ O ₄ is extracted from the Freon as KNO ₂ and KNO ₃ with aqueous KOH. The KNO ₂ is converted to N ₂ and K ₂ SO ₄ by sulfamic acid. The excess KOH is neutralized with nitric acid to produce an innocuous KNO ₃ solution. The concentration of N ₂ O ₄ left in the treated Freon is below the detection limit of the analytical method used. It was discovered that N ₂ O ₄ reacts with Freon over time to produce halogenated nitroethanes. The reactor has ben delivered to the Western Space and Missile Center (WSMC)				
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INTRODUCTION

Freon (throughout this report Freon refers to Freon 113) is used at the Western Space and Missile Center (WSMC) to flush nitrogen tetroxide (N_2O_4) from the lines in the oxidizer handling areas. Freon was chosen to flush the lines because it readily dissolves N_2O_4 . The resulting solution is a hazardous waste because it is now corrosive and contains the oxidizer N_2O_4 . Solvent reclaimers, acceptable to WSMC, will not accept Freon containing N_2O_4 . The waste Freon was accumulating at WSMC which prompted the personnel at WSMC to ask for help. In December 1989, the Bio-environmental Office at OLAC Phillips Laboratory was asked to develop a process to extract the N_2O_4 from the waste Freon. The Bio-environmental Office brought the problem to the Chemistry Branch of the Fundamental Technologies Division. The author volunteered to investigate the problem.

Bench scale tests were conducted on freshly prepared Freon and N_2O_4 solutions. It was shown that aqueous caustic would extract the N_2O_4 from the Freon. If the caustic was potassium hydroxide (KOH), then the N_2O_4 formed potassium nitrate (KNO_3) and potassium nitrite (KNO_2) as it was extracted. The KNO_2 will react with acids to release oxides of nitrogen. Attempts to oxidize the KNO_2 to KNO_3 failed, therefore, other methods of removing the KNO_2 were investigated. The method chosen was to convert the KNO_2 to nitrogen gas (N_2) using sulfamic acid (HSO_3NH_2).

Preliminary results were presented at WSMC in February 1990. A sketch of a reactor design was presented and discussed. WSMC personnel suggested that the reactor use no electrical components and that the unit be portable. Because electric refrigeration could not be used, adding ice to the aqueous layer was the cooling method chosen. These factors were incorporated into the final reactor design.

The reactor was designed to be assembled from commercially available components. The reactor body was a 72 gallon stainless steel tank purchased from Viatic. The tank came with a lid which proved to be too thin to support the heavy components to be mounted on it. A new lid was designed and fabricated. A completely sealed magnetic level indicator was purchased from IMO Industries, Inc. An air-powered motor (Trade name, "Lightnin"^(R)) was purchased from J. W. Leser Co. The stainless steel ball valves were purchased from Motion Industries. The reactor components were assembled at the OLAC Phillips Laboratory.

The reactor was ready for field tests in early 1992. The operating instructions and the test plan were discussed at a meeting at WSMC in March of 1992. WSMC personnel indicated that since obtaining a permit for the field test would cause a considerable delay, they suggested that the test be performed at the OLAC Phillips Laboratory. When it was discovered that there were no ice machines at the proposed test area at WSMC, the issue was raised could liquid nitrogen be substituted for ice during the field tests?

The field tests were moved to OLAC Phillips Laboratory. The reactor tests were conducted in late May 1992. After the Freon was processed through the reactor, the third phase of the project began. The third phase involved analyzing the reactor products and investigating the causes of the anomalous results that occurred when the process moved from bench scale to full scale. It was discovered that N_2O_4 will react with Freon during long-term storage of the solution. This reaction produces nitro-derivatives of Freon. It was observed that black iron pipe and fittings used on the

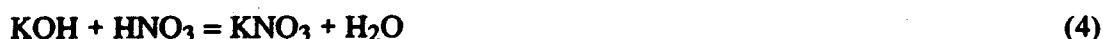
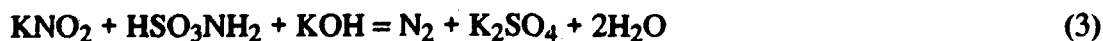
reactor corroded and transferred ferric iron to the KOH solution turning it yellow. This caused some confusion during the field tests as the yellow color was attributed to hexavalent chromium. The reactor was delivered to WSMC in July 1992.

EXPERIMENTAL

Process Development

The process chemistry was developed on the bench scale using standard laboratory equipment. Nitrogen tetroxide will react with aqueous KOH to produce KNO_2 and KNO_3 (Eqn. 1). The N_2O_4 in the waste Freon can be extracted by intimately mixing the Freon with aqueous KOH. Because water and Freon are not miscible, the transfer of N_2O_4 from the Freon to the water can only occur at the interface of the two liquids. Since KNO_2 will release oxides of nitrogen in acid, it was necessary to remove KNO_2 to produce a stable aqueous product. A mixture of KOH and hydrogen peroxide (H_2O_2) was used to extract the N_2O_4 from freshly prepared Freon/ N_2O_4 solutions. The N_2O_4 was expected to oxidize the KNO_2 to KNO_3 as it formed. Analysis of the Freon showed that all the N_2O_4 has been removed, but analysis of the aqueous showed a high residual KNO_2 concentration. Nitric oxide and nitrogen dioxide will react in aqueous base to produce Nitrite (Eqn. 2). The failure of H_2O_2 to oxidize KNO_2 to KNO_3 prompted the search for another way to eliminate KNO_2 from the aqueous. The reaction of nitrites with sulfamic acid is reported in the literature as being quantitative. [2] The final process chemistry consists of two steps. First, the N_2O_4 is extracted from the Freon with aqueous KOH, the the aqueous is treated with solid sulfamic acid to convert the KNO_2 to nitrogen gas (Eqn. 3). To ensure complete extraction of N_2O_4 from the Freon, an excess of KOH is used. This excess KOH must be neutralized with nitric acid to bring the pH of the aqueous within permissible discharge limits (Eqn. 4).

Freon is a volatile liquid (b.p. 47.6°C) and the chemical reactions used to extract the N_2O_4 are exothermic, therefore, cooling is necessary to prevent the loss of Freon by evaporation. The method chosen to cool the extraction process was to add ice to the aqueous KOH. The process is summarized in the following equations:



The reactor uses a feed-forward control of the process chemistry. The control process is based on the N_2O_4 content of the Freon expressed in weight percent. The amount of KOH required is calculated using Equation 5.

$$\text{lbs of KOH} = \text{gallons of Freon} \times \text{wt.\% N}_2\text{O}_4 \times 0.176 \quad (5)$$

The factor 0.176 contains all of the conversion factors plus a 10% excess. The amount of sulfamic acid needed to react with the KNO_2 in the spent aqueous is calculated using Equation 6.

$$\text{lbs of sulfamic acid} = \text{total volume of Freon treated} \times \text{wt.\% N}_2\text{O}_4 \times 0.139 \quad (6)$$

The Freon volume is measured in gallons and the factor 0.139 contains all of the conversion factors.

Analytical Techniques

Ultraviolet-visible spectroscopy was used to analyze the aqueous solutions for KNO_3 and KNO_2 . The nitrite ion was found to absorb at 356 nm and the nitrate ion was found to absorb at 303 nm. The UV-visible spectrum of N_2O_4 in Freon has a maximum absorbance at 342 nm. The detection limit for N_2O_4 in Freon was determined to be 0.5 ppm. UV-Vis was used to analyze all Freon solutions for dissolved species.

Trace metals in the aqueous were determined by Inductively Coupled Plasma Emission Spectroscopy (ICP) using an ARL Fisons model 3410 ICP. The ICP was used in the qualitative scanning mode to determine which elements were present, but not their concentrations.

Wet chemical or "spot tests" were used to detect the presence of CrVI and FeIII. Hexavalent chromium can be detected by adding a drop of diphenylcarbazide in acetone to the acidified sample. The solution turns violet if CrVI is present. If the sample is made acidic with nitric acid and thiocyanate solution is added, a red color shows the presence of ferric iron.

Reactor Test

The reactor was set up in an elevated containment tank. The Freon feed system shown in Figure 1 was set up next to the reactor and connected to it by a length of rubber hose. The Freon feed system uses a carefully controlled amount of compressed air to force the contaminated Freon out of the drum and into the reactor.

WSMC sent two drums of contaminated Freon to the Phillips Laboratory for the reactor tests. The total volume of contaminated Freon was 110 gallons. The Aerospace Fuels Laboratory at WSMC reported that the Freon contained 0.14 wt. % N_2O_4 .

The reactor was prepared for processing the contaminated Freon. See Figure 2 for the location of the valves and other components of the reactor. When all of the valves were closed, the porthole was opened. Approximately 15 gallons of tap water was added to the reactor, the volume was estimated by the 6 inch rise of the level indicator. Approximately 96 quarts of ice was added to the reactor through the porthole. To determine the amount of KOH required, Equation 5 was multiplied by 1.176 to compensate for the 85% minimum purity of the KOH supply. The required amount of KOH (1450 grams) was weighed out and added to the reactor. The mixer was run for 5 minutes to dissolve the KOH. The reactor was now ready to receive the first batch of contaminated Freon.

The Freon drums were removed from their overpacks. A MDA TLD toxic gas detector was placed on top of one of the drums to measure the NO_2^* released when the bungs were removed. The Freon feed system (Fig.1) was installed on the first drum. The Freon feed system was connected to valve A. Valve A was opened to allow Freon into the reactor and valve B was opened to vent the reactor. The drum was carefully pressurized.

*** N_2O_4 exists in equilibrium with NO_2 , the proportion of NO_2 increases as temperature increases and as pressure decreases.**

The pressure required to force the Freon out of the drum caused the top of the drum to bulge. Freon was fed into the reactor until the level indicator had risen 12 inches above the level established by the KOH solution. When the Freon loading operation was completed, Valve A was closed. The MDA TLD Toxic gas detector was positioned to measure any NO₂ venting from Valve B. The Lightnin (®) mixer was run for 5 minutes, then the phases were allowed to separate for 5 minutes. Valve C was opened to sample the Freon layer. The Freon sample was labeled as F2. The treated Freon was drained into a clean drum. The level indicator was used to assure that only 11 of the 12 inches of Freon was drained from the reactor. This prevented water from contaminating the treated Freon.

As the second batch of Freon was fed into the reactor a problem developed. Compressed air laden with NO₂ escaped the feed system, flowed through the reactor and out of the vent. The NO₂ laden air escaped from the feed system via the dip tube when the liquid level dropped below it. The air supply to the feed system was shut off and the test personnel evacuated upwind until the NO₂ had cleared. The second batch of Freon was then processed exactly like the first. The sample of the second batch of treated Freon was labeled F3. The first drum was disconnected from the feed system and rebunged. Several gallons of contaminated Freon had to be left in the drum because the feed system could not reach it.

To test if liquid nitrogen (LN₂) could be used as a coolant, several liters of LN₂ were added to the reactor before the third batch of Freon was processed. The LN₂ was added via the porthole which was left open to accommodate the large volume of nitrogen vapor produced. The feed system was connected to the second drum of contaminated Freon. Approximately 27 gallons of Freon were transferred to the reactor. During the mixing operation, the porthole was opened so that the mixing pattern inside the reactor could be observed. Appropriate PPE was worn for this operation. The treated Freon was drained from the reactor and sampled. The sample was labeled F4.

The fourth batch of Freon was the smallest because the filling operation was stopped before the Freon level could drop below the end of the dip tube. Five minutes was allowed for both mixing and phase separation. The Freon was sampled and labeled F5. When the last of the treated Freon was drained from the reactor, it was collected in a 4-liter beaker along with some of the aqueous. The aqueous was decanted off the top of the Freon back into the reactor. The aqueous had turned yellow during the extraction process. The aqueous was drained into one of the overpack drums for further treatment. The aqueous was sampled and labeled A1.

It was assumed that the yellow color in the aqueous was caused by hexavalent chromium, therefore, ferrous ammonium sulfate was added as a reducing agent. Chromium III is much less hazardous than CrVI. The amount of sulfamic acid required to react with the KNO₂ in the aqueous was calculated using Equation 6. Two 500-gram bottles of sulfamic acid were added to the aqueous.

After the reaction stopped, the solution was sampled and labeled A2. The pH of the solution was measured with ColorpHast(®) pH indicating strips. Nitric acid was mixed into the KOH solution in small amounts and the pH was checked after each addition until the pH was between 6 and 7. The neutralized aqueous was sampled and the sample was labeled A3. The aqueous was covered so that the solids could settle. The Freon and aqueous samples were analyzed. The analysis of the aqueous (A3) showed a decrease in the KNO₂ concentration but some KNO₂ still remained. The aqueous in the drum was treated with 250 grams of sulfamic acid. After the reaction stopped, a sample was taken and labeled A6. The addition of sulfamic acid to the aqueous dropped its pH out of the permissible discharge range. Magnesium hydroxide was stirred into the aqueous until a pH of 7 was achieved. After the solids settled and the aqueous (A6) analysis showed no KNO₂ or CrVI, the

KNO_3 and K_2SO_4 solution was syphoned off and dumped. The solids which were mostly $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$ were air dried and discarded.

Post Reactor Test Analysis

The reactor tests produced some results that would not have been anticipated from the results of the bench scale tests. The aqueous turned yellow which required the use of wet chemical and spectrographic techniques to determine the cause. Analysis of the treated Freon showed an unexplained absorbance peak near 280 nm. A series of experiments were conducted to determine what produced this absorption.

A 250 ml. separatory funnel with vigorous hand shaking was used to simulate the operation of the reactor. A concentrated aqueous NaNO_2 solution was added to the separatory funnel then 40 ml. of clean Freon was added. The two liquids were shaken together for 10 minutes then were allowed to separate. The Freon was analyzed, returned to the funnel, shaken with NaNO_2 solution for 10 minutes, allowed to separate and reanalyzed. This procedure was repeated with a NaNO_3 solution. The separatory funnel was cleaned and dried. Clean Freon was added to the funnel then 5 ml. of isopropanol and finally 50 ml. of 10% aqueous nitric acid. This mixture was shaken for 10 minutes and allowed to separate, and then the Freon layer was analyzed. A dilute solution of MON-3 in Freon was shaken with chilled KOH solution for 15 minutes. The layers were allowed to separate and the Freon was analyzed. Freon solutions of 1-nitropropane, 2-nitropropane, and 1,1-dinitroethane were prepared and their UV-Visible spectra were recorded.

Results

Potassium hydroxide and H_2O_2 mixtures extracted N_2O_4 from Freon completely. The analysis of the aqueous extraction solutions showed a high residual KNO_2 concentration. The H_2O_2 had failed to oxidize all the KNO_2 to KNO_3 . In the two step process, the sulfamic acid treatment eliminated all of the KNO_2 in the aqueous.

The NO_2 emissions from the reactor tests were extremely low except for Batch 2. When the drums were opened, the maximum concentration of NO_2 measured was 2.4 ppm. No NO_2 could be detected at the reactor vent when the first, third and fourth batches of Freon were processed. The sparging that occurred when Batch 2 was fed into the reactor exceeded the detector's maximum reading of 9.0 ppm.

The spot tests performed on the aqueous labeled A1 were negative for hexavalent chromium and positive for ferric iron. ICP emission spectroscopy detected Zn, Fe, Ca, K, Al, Na, and B in the aqueous. When the aqueous was acidified, the yellow color was discharged but reappeared when the solution was made alkaline again.

Figure 3 shows the UV-Visible spectrum of A1 (the untreated aqueous) from the reactor. Figures 7 and 8 show the spectra of NaNO_2 and NaNO_3 , respectively. Comparing Figure 3 with Figures 7 and 8 demonstrates that the untreated aqueous contained both KNO_2 and KNO_3 . In figure 3, the peak at 360.5 nm was attributed to KNO_2 and the peak at 300.5 nm was assigned to KNO_3 . Figure 4 shows the spectrum of the aqueous A2 after it had been treated with ferrous ammonium sulfate and then sulfate acid. The shoulder near 350 nm indicates that some KNO_2 still remains. Figure 5 shows the spectrum of A3 (the neutralized aqueous), residual KNO_2 is still evident. The spectrum A6 (the aqueous after the second sulfamic acid treatment) is shown in Figure 6. The

spectrum clearly shows that all the KNO_2 was destroyed. Figure 9 shows the spectrum of the contaminated Freon received from WSMC. The peak at 341.5 nm was assigned to N_2O_4 , which is consistent with prior experience. Figures 10–13 show the spectra of the four batches of treated Freon. Figures 9–13 are combined in Figure 14 for comparison. The spectra demonstrate that all of the N_2O_4 was extracted from the Freon. The peak near 275 nm in Figures 10–13 is due to compounds such as 1-nitro-2, 2-dichloro-1,1, 2-trifluoroethane produced by the reaction of NO_2 with Freon.

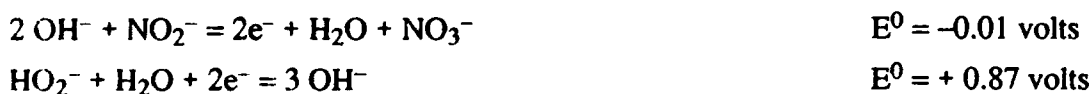
Figure 15 shows the spectrum of Freon that was contaminated with MON-3 then immediately extracted with aqueous KOH. The absence of peaks at 342 nm and 275 nm shows that the N_2O_4 was completely extracted without leaving any UV-absorbing species in the Freon.

The reaction between Freon, isopropanol, and dilute nitric acid produced a spectrum without any distinct peaks, instead, the absorbance began increasing at 280 nm and was off the scale at 220 nm. The spectrum did not have the peak at 275 nm which can be seen in Figures 10–13.

Figure 16 shows the spectrum of Freon that was repeatedly contacted with aqueous NaNO_3 . The spectrum of Freon contacted with NaNO_2 is shown in Figure 17. Neither the NaNO_3 nor NaNO_2 transferred to the Freon. Figure 18 shows the UV-Visible spectrum of 1-nitropropane in Freon and the spectrum of Batch 3 of treated Freon for comparison. Figure 19 shows two spectra of MON-3 in Freon, one is the untreated Freon from WSMC and the other solution was made up just before the spectrum was recorded. The Freon from WSMC has a lower absorbance at 343 nm and a higher absorbance at 280 nm.

DISCUSSION

The mixture of KOH and H_2O_2 was chosen originally because thermodynamic calculations had shown that the oxidation of nitrite to nitrate by alkaline H_2O_2 was highly favorable. ⁽¹⁾



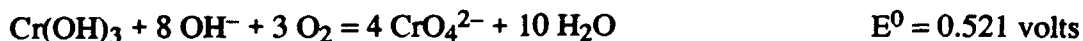
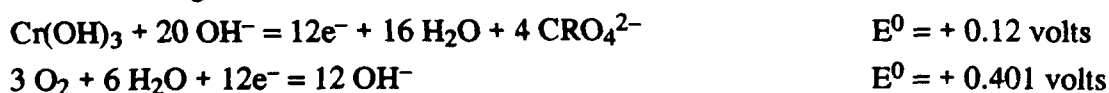
$$\text{Since } \Delta G^0 = -n F E^0$$

$$\Delta G^0 = -(2) (23.05 \text{ Kcal/volt}) (0.86 \text{ volts}) = -39.6 \text{ Kcal}$$

Although the reaction has a large driving force, i.e., $\Delta G^0 < 0$, it is kinetically inert or is slow to be of any practical use.

The reaction of nitrite ions with sulfamic acid is quantitative, ⁽²⁾ therefore, sulfamic acid can be relied upon to destroy all the KNO_2 in the aqueous extraction product. Some N_2O_3 can form in a side reaction that increases with nitrite concentration. Since N_2O_3 will react with KOH to form KNO_2 , very little N_2O_3 could be released if the sulfamic acid is added to an alkaline solution. Equation 2 shows that MON-3 would produce a higher proportion of KNO_2 than pure N_2O_4 would during the extraction process. The parameter 0.139 in Equation 5 is based on pure N_2O_4 reacting with KOH. MON-3 would produce about 10% more KNO_2 than pure N_2O_4 . The N_2O_3 forming side reaction and that the fact that MON-3 was the form of N_2O_4 used in the test both increased the amount of sulfamic acid needed to completely destroy the KNO_2 .

The assumption that the yellow color in the aqueous was due to hexavalent chromium was based on the following electrochemical data. [2]



The free energy for the reaction is -36 Kcal/mole of chromium. The passive layer that makes stainless steel corrosion resistant is chromium sesquioxide, this oxide layer was assumed to be the source of chromium. The assumption proved to be wrong as both ICP emission spectroscopy and the diphenylcarbazide test failed to find any chromium in the aqueous. The yellow color in the aqueous was due to colloidal hydrous ferric oxide. The iron came from the black iron pipe and fittings used. The fact that HNO_3 caused the yellow to disappear and that the color reappeared when the solution was made alkaline suggests an oxide or hydroxide. The other elements found in the aqueous by ICP do not normally form colored compounds.

The sparging problem with Batch 2 was caused by pressurizing the drum. Once the liquid level dropped below the end of the dip tube, the gases in the head space could flow up the dip tube and into the reactor where the large bubbles of NO_2 would rise through the aqueous too quickly to react. A feed system that did not pressurize the drum, such as a gravity feed system, would eliminate this problem.

Figure 2 shows the internal structure of the reactor. The contaminated Freon is fed into the reactor through Valve A. Because the level of the aqueous KOH solution is initially above the end of the feed pipe, the contaminated Freon enters the reactor under the KOH solution. This prevents the escape of any N_2O_4 during loading except when sparging occurs. This design proved to be highly effective as no NO_2 was released during normal operation.

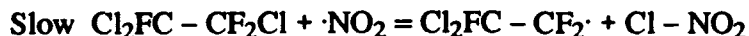
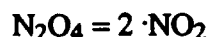
Figure 20 shows the flow pattern of the phases inside the reactor in a simplified form. Only axial flows are shown because the reactor was designed to favor axial flow. The baffles attenuate any tangential flow and radial flow is suppressed by the type of impeller used. The difference in density of the two liquids alters the flow pattern. When water is drawn into the Freon, it immediately begins to decelerate because of the negative acceleration due to gravity, i.e., it wants to float. When Freon is lifted into the water layer, gravity tends to accelerate it downwards, i.e. it wants to sink. These flow patterns tend to keep the two phases stratified. With an almost continuous aqueous layer over the Freon, it is not possible for any NO_2 to escape. This was clearly demonstrated with batches 1, 3, and 4. When the mixing was observed through the porthole, the surface was relatively calm with evenly distributed small eddies.

The extraction of N_2O_4 by KOH occurs at the interface between the water and Freon. For the extraction to proceed at a useful rate, the interfacial area must be increased by breaking up one or both phases into fine drops. Since most of the droplets form at the impeller [3] most of the extraction occurs at the impeller or downstream from it. Since the extraction process is diffusion controlled, the higher the original N_2O_4 concentration in the Freon, the longer it will take to extract it. In a process that depends on diffusion of a reactant to the surface of a droplet, the process can be accelerated by decreasing the size of the droplet. Therefore, a higher initial N_2O_4 concentration can be compensated for by increasing the impeller speed. [3]

The peaks at 275 nm in Figures 10 - 13 are the results of NO_2 reacting with Freon to form halogenated nitroethane compounds. Figures 16 and 17 show that NaNO_2 and NaNO_3 solutions do

not transfer the salts to Freon even with vigorous mixing. Figure 15 shows that freshly prepared N_2O_4 (MON-3) Freon solutions can be extracted with aqueous KOH to produce clean Freon with no absorbance at 275 nm. Figure 18 shows the spectrum of one of the batches of treated Freon and the spectrum of 1-nitropropane. Figure 19 shows that MON-3 dissolved in Freon undergoes a chemical change with time that increases its absorbance at 280 nm and decreases its absorbance at 342nm.

Nitrogen dioxide is a free radical molecule and can initiate free radical reactions. [4] The following mechanism is proposed to explain the formation of halogenated nitroethanes:



If impurities that contain hydrogen atoms are present in the Freon, the impurities will undergo the reaction much faster. The close match of the two spectra in Figure 18 and a plausible chemical mechanism for the formation of halogenated nitroethanes support the conclusion that the treated Freon is contaminated with halogenated nitroethanes.

There may be halogenated nitroethanes in the aqueous KOH used to treat the contaminated Freon. The aqueous was not analyzed for halogenated nitroethanes. Figure 14 suggests that some of the halogenated nitroethanes transferred to the aqueous. The absorbance at 275 nm increases with each batch of Freon treated indicating that the aqueous is approaching saturation with respect to the UV-absorbing species.

CONCLUSIONS

- (1) The reactor efficiently and completely extracts N_2O_4 from Freon and N_2O_4 solution.
- (2) When the reactor is operated properly, no NO_2 emissions are released.
- (3) The treated Freon still contains halogenated nitroethanes derived from NO_2 reacting with Freon.
- (4) The KOH solution used to extract the N_2O_4 , was discolored by hydrous ferric oxide.
- (5) More than the calculated amount of sulfamic acid was needed to destroy all of the KNO_2 in the extraction solution.

RECOMMENDATION

- (1) Use a gravity system to load the contaminated Freon into the reactor.
- (2) If liquid nitrogen is used as the coolant, it should be added through the porthole. The porthole must remain open to vent the large volume of nitrogen vapor generated.
- (3) All fittings and pipings must be made of stainless steel.
- (4) The halogenated nitroethanes may not be thermally stable, therefore, great care should be exercised when distilling the reclaimed Freon.

REFERENCES

- (1) R. C. Brasted, Analytical Chemistry, 24, 1952, p. 1111.
- (2) R. C. Weast, editor, CRC Handbook of Chemistry and Physics 57th Ed., CRC Press, Cleveland, Ohio, 1976, p. D-142.
- (3) D. S. Azbel and N. P. Cheremisinoff, Fluid Mechanics and Unit Operations, Ann Arbor Science, 1983, p. 708.
- (4) J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, McGraw-Hill, New York, 1968, p. 548.

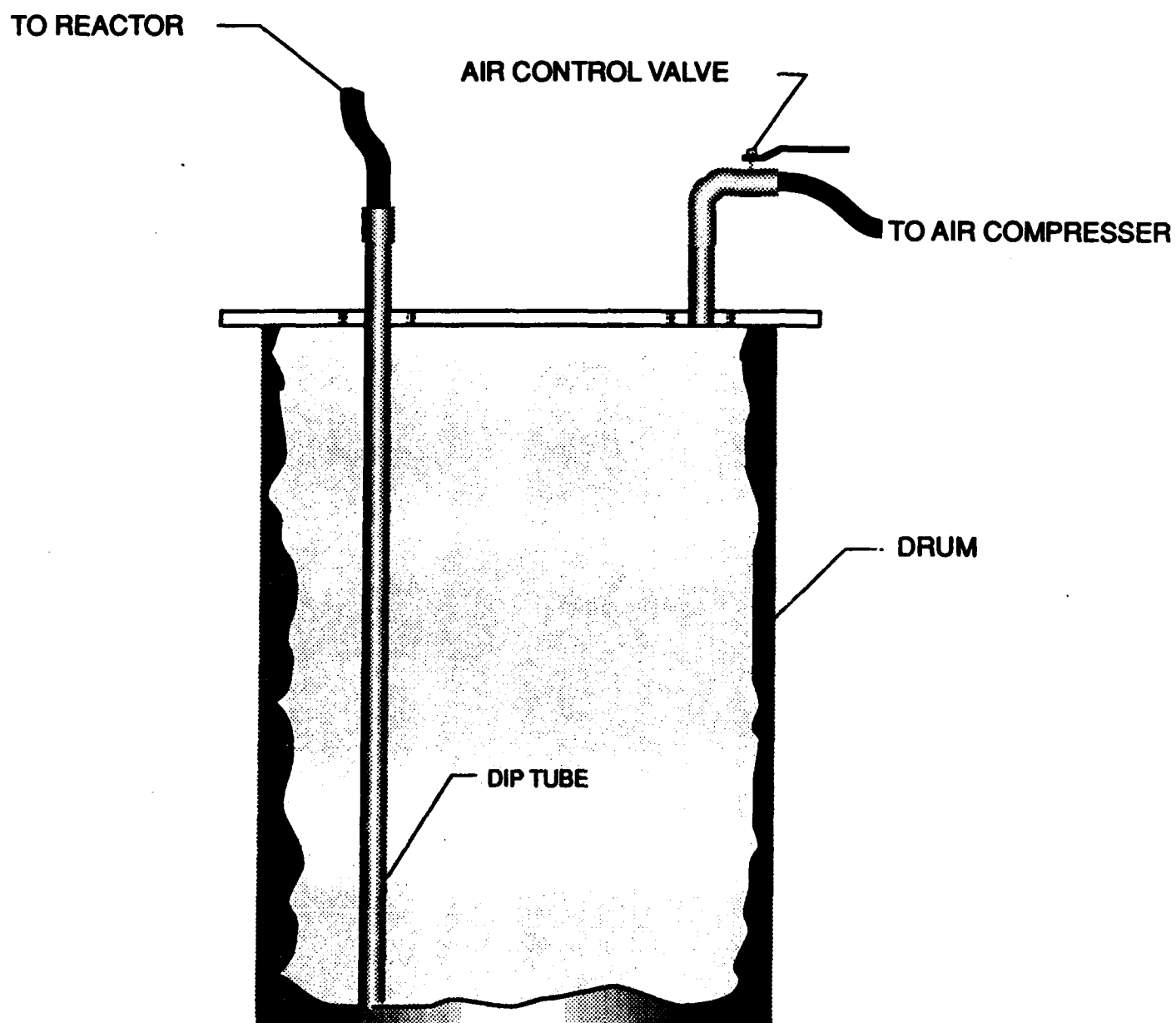


Figure 1 The Freon Feed System

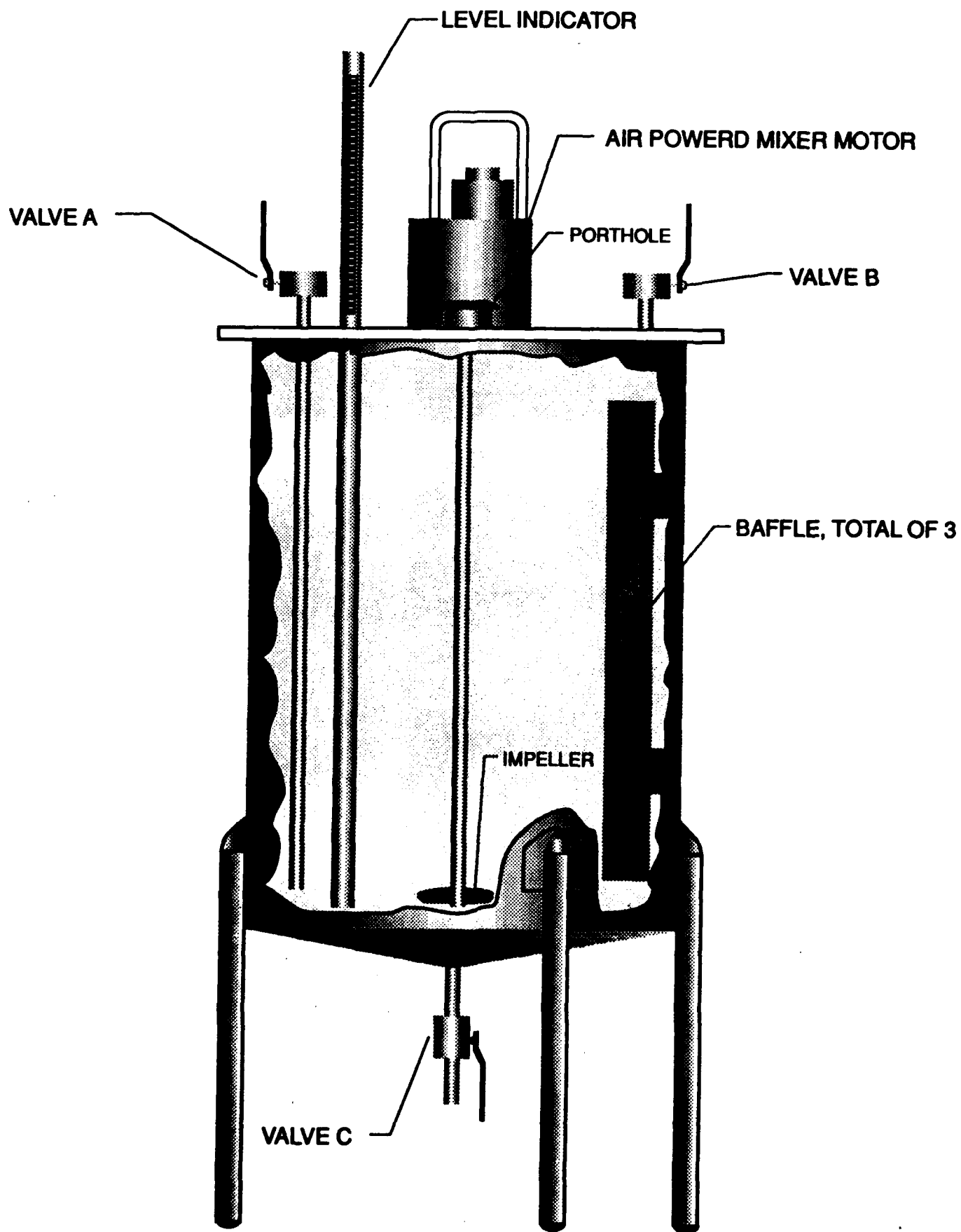
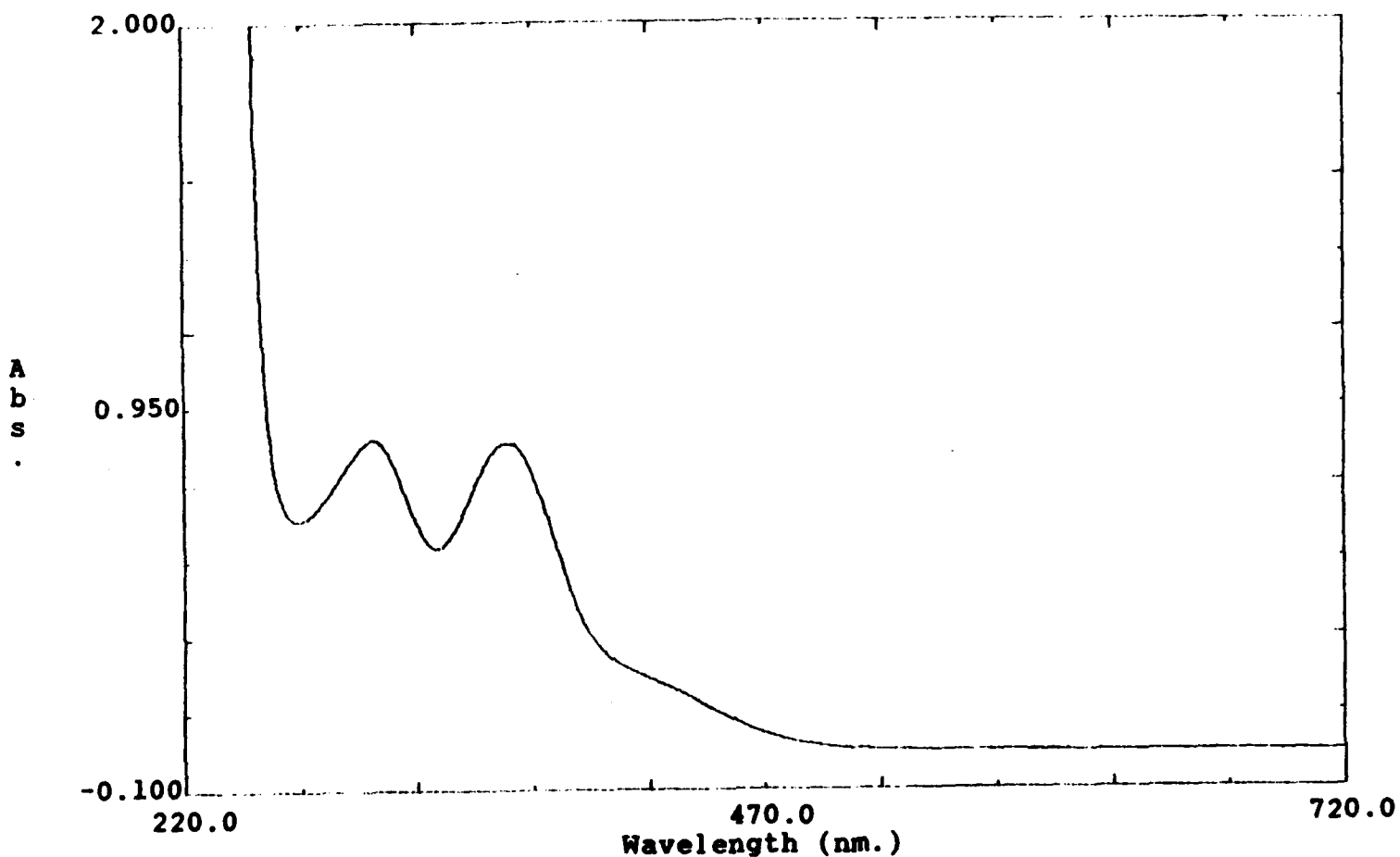


Figure 2 Schematic of Freon/N₂O₄ Reactor



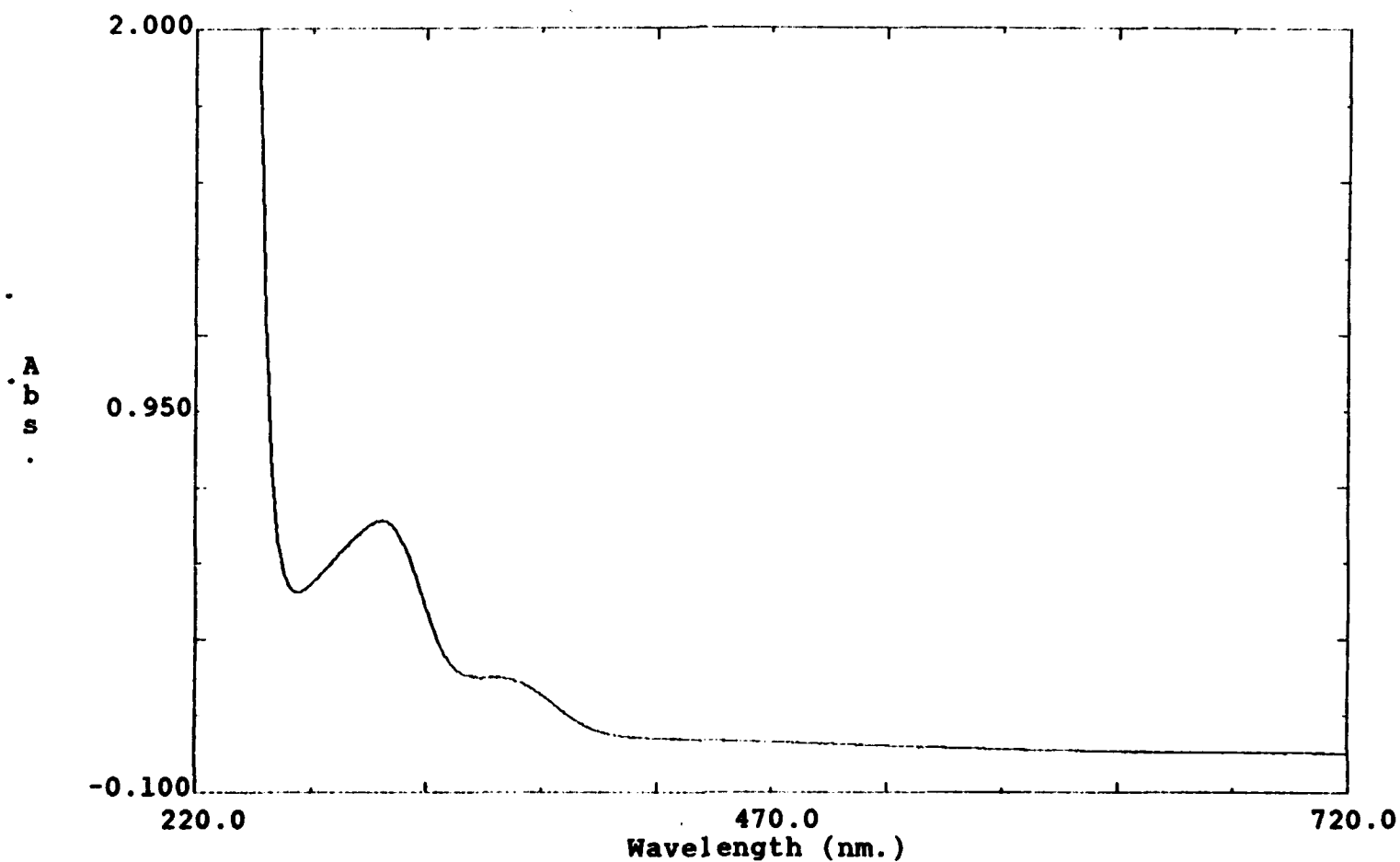
File Name: al
untreated aqueous from reactor

No.	Peak Pick Wavelength (nm.)	Abs.
1	360.50	0.852
2	300.50	0.863

Created: 13:50 05/26/92
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Figure 3.
Spectrum of the untreated
aqueous from the reactor.

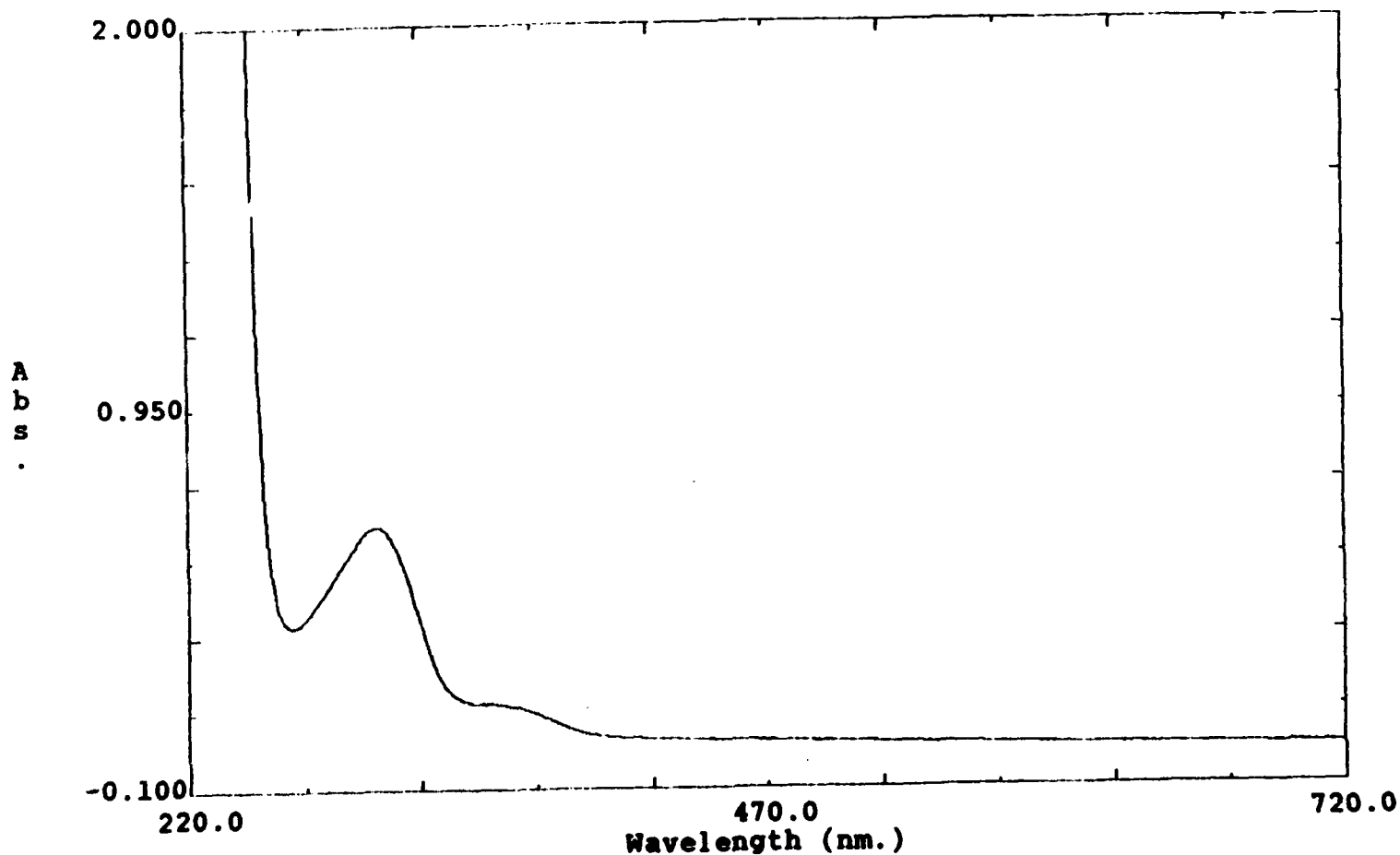


File Name: a2
 aqueous treated with Fe(2) and
 sulfamic acid
 Created: 13:59 05/26/92
 Data: Original

Peak Pick		
No.	Wavelength (nm.)	Abs.
1	697.00	0.011
2	300.50	0.649

Measuring Mode: Abs.
 Scan Speed: Medium
 Slit Width: 0.5
 Sampling Interval: 0.5

Figure 4. Spectrum of the aqueous from the reactor after treatment with ferrous iron and sulfamic acid.



File Name: a3

final aqueous

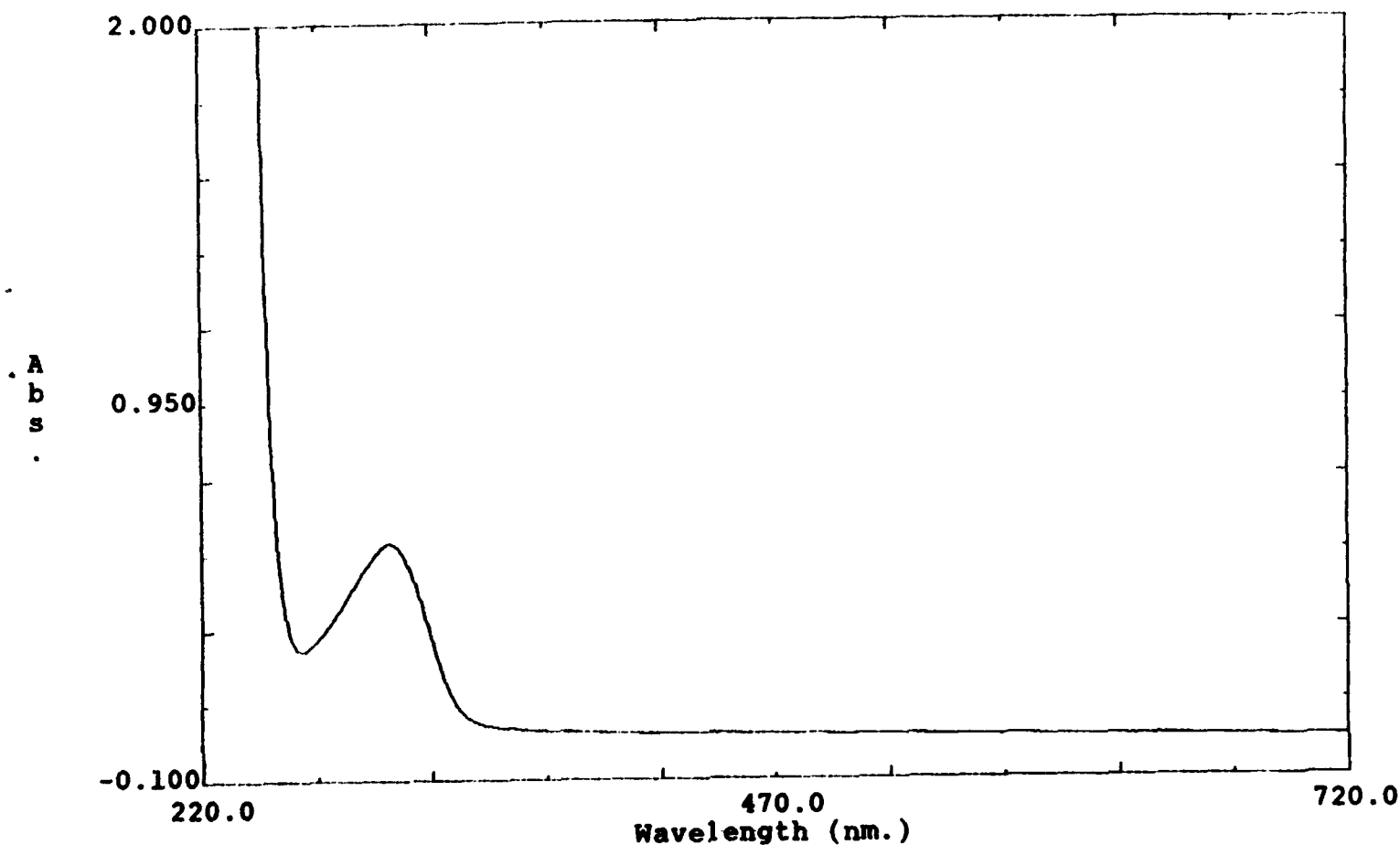
Created: 14:08 05/26/92

Data: Original

Measuring Mode: Abs.
 Scan Speed: Medium
 Slit Width: 0.5
 Sampling Interval: 0.5

No.	Peak Pick Wavelength (nm.)	Abs.
1	300.50	0.626

Figure 5. The spectrum of the "Final aqueous."

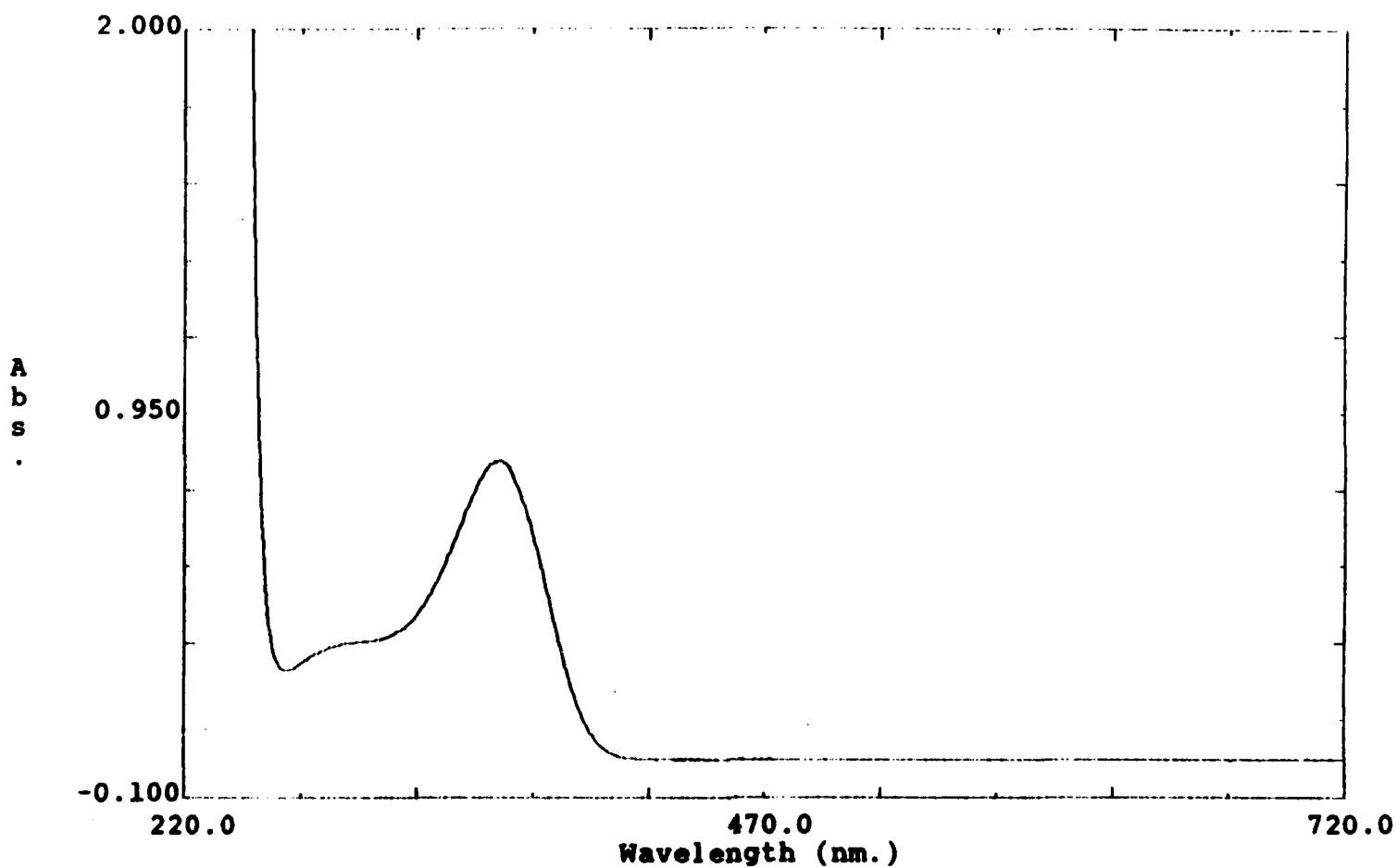


File Name: a6
 Final aqueous treated with
 additional sulfamic acid
 Created: 09:19 05/27/92
 Data: Original

No.	Peak Pick Wavelength (nm.)	Abs.
1	301.50	0.562

Measuring Mode: Abs.
 Scan Speed: Medium
 Slit Width: 0.5
 Sampling Interval: 0.5

Figure 6. Spectrum of the Final aqueous after treatment with additional sulfamic acid.



File Name: a4

sodium nitrite

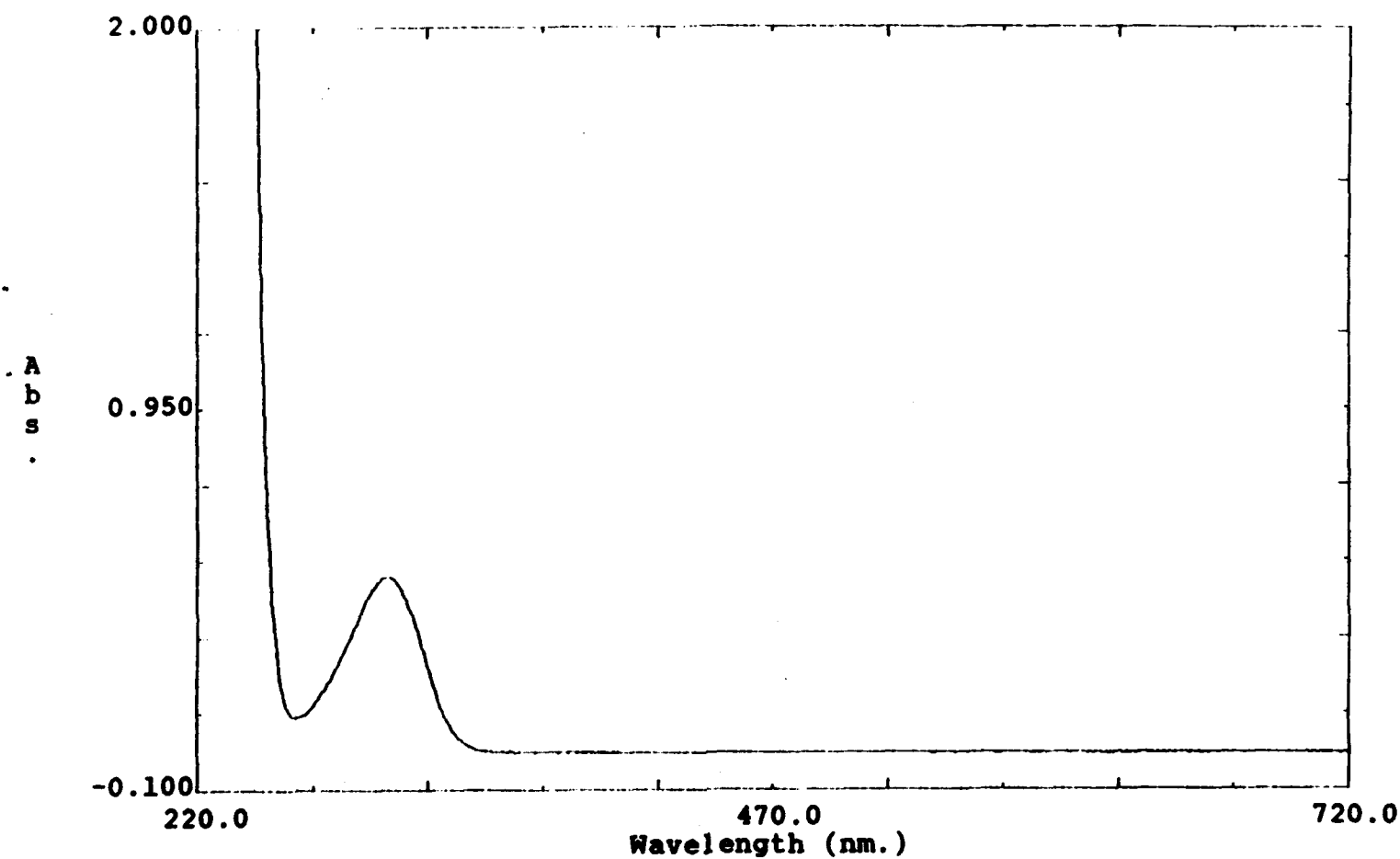
Created: 14:39 05/26/92

Data: Original

Measuring Mode: Abs.
 Scan Speed: Medium
 Slit Width: 0.5
 Sampling Interval: 0.5

Peak Pick		
No.	Wavelength (nm.)	Abs.
1	704.00	0.004
2	356.00	0.823

Figure 7. Spectrum of aqueous sodium nitrite.



File Name: a5

sodium nitrate

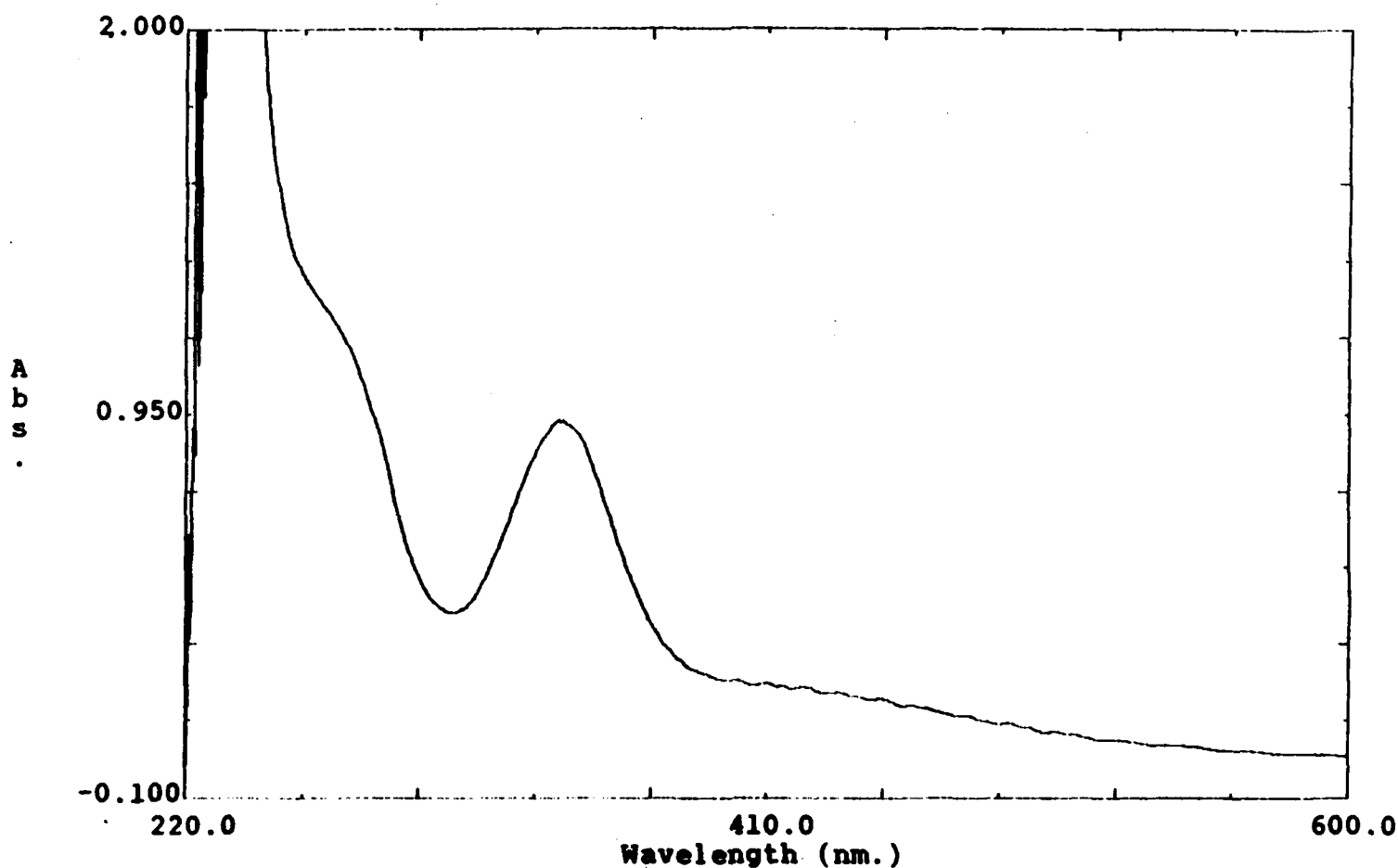
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Data: Original

Measuring Mode: Abs.
 Scan Speed: Medium
 Slit Width: 0.5
 Sampling Interval: 0.5

No.	Peak Pick Wavelength (nm.)	Abs.
1	496.50	0.003
2	303.00	0.488

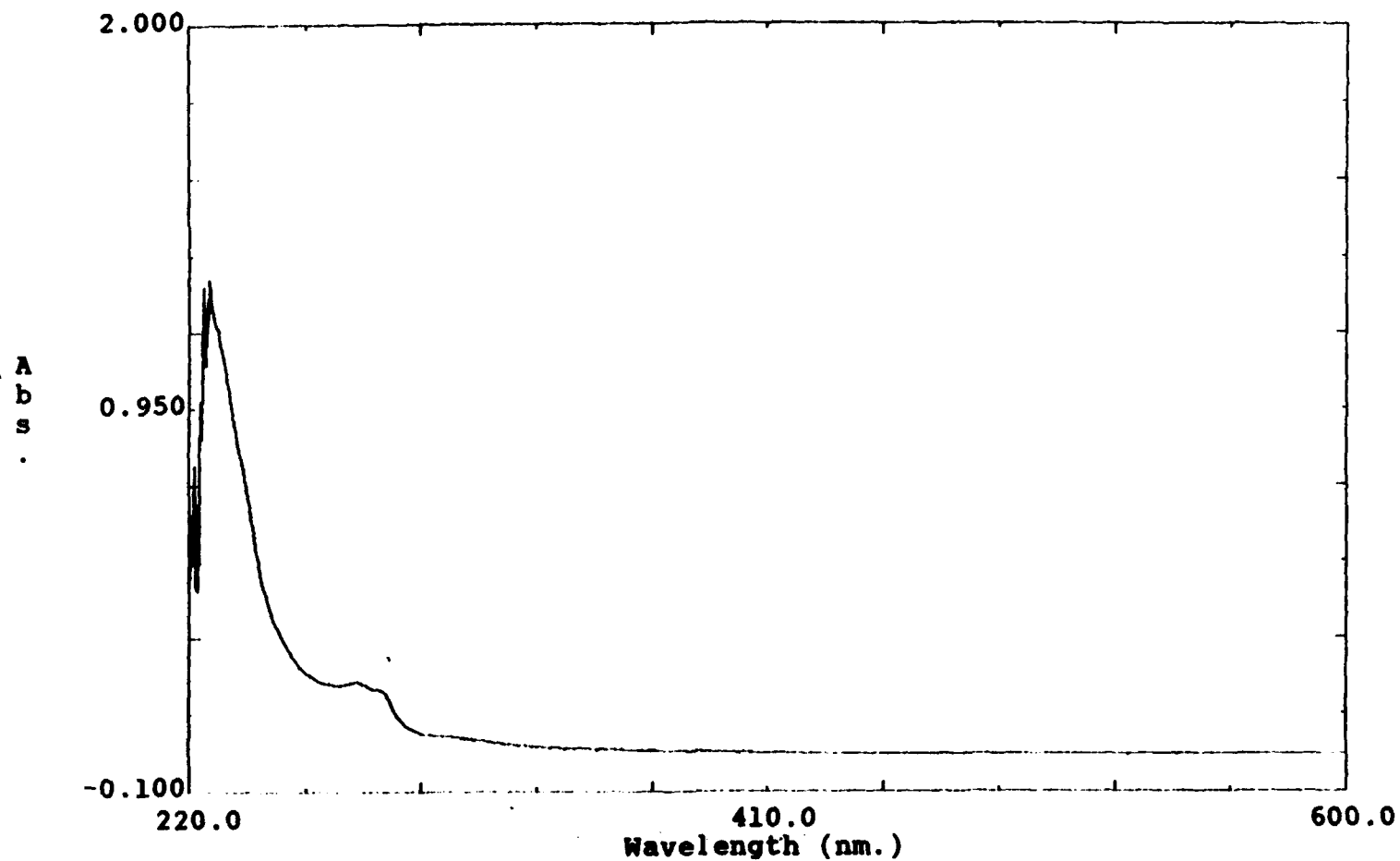
Figure 8. Spectrum of aqueous sodium nitrate.



File Name: fs2
 second sample of untreated
 freon
 Created: 12:42 05/26/92
 Data: Original
 Measuring Mode: Abs.
 Scan Speed: Medium
 Slit Width: 0.5
 Sampling Interval: 0.5

Peak Pick		
No.	Wavelength (nm.)	Abs.
1	540.50	0.045
2	505.00	0.081
3	489.00	0.105
4	447.00	0.171
5	433.50	0.189
6	421.00	0.202
7	410.50	0.213
8	341.50	0.936

Figure 9. Spectrum of the untreated Freon.



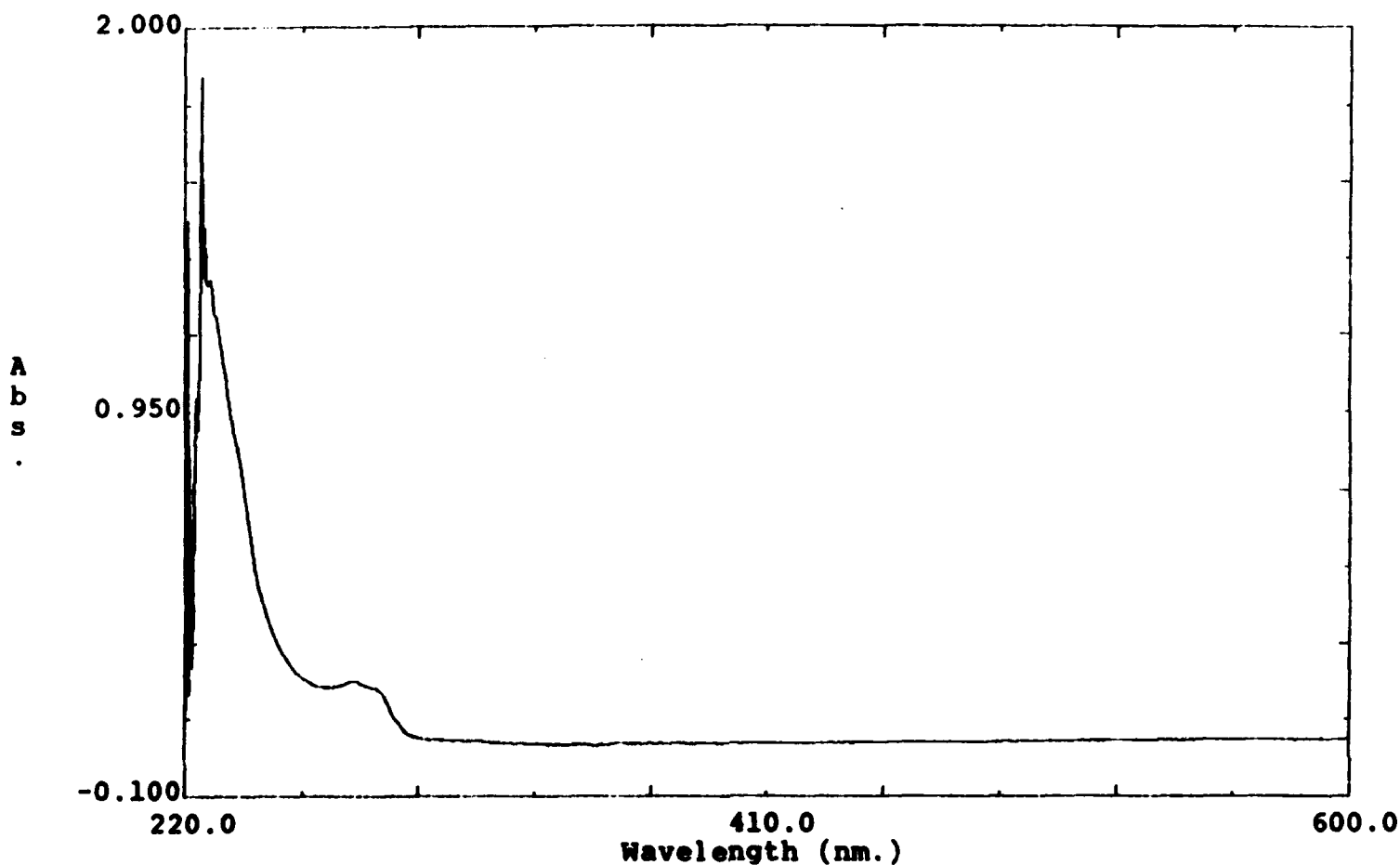
File Name: f2

Peak Pick		
No.	Wavelength (nm.)	Abs.
1	274.50	0.202

Created: 10:56 05/26/92
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Figure 10. Spectrum of the first batch of treated Freon.



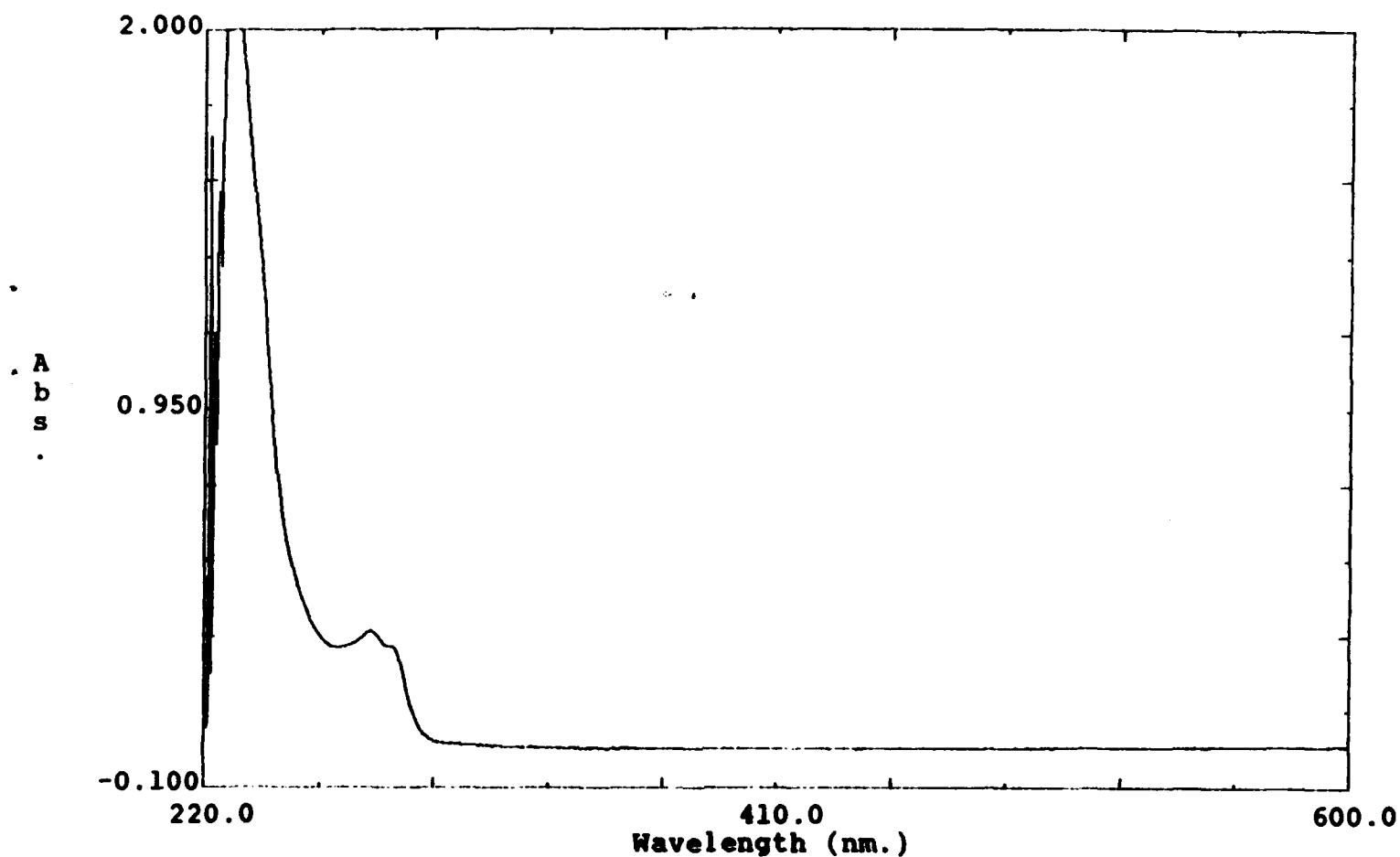
File Name: f3

Created: 11:03 05/26/92
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Peak Pick		
No.	Wavelength (nm.)	Abs.
1	591.00	0.058
2	572.50	0.058
3	425.50	0.047
4	363.00	0.046
5	275.00	0.218

Figure 11. Spectrum of the second batch of treated Freon.



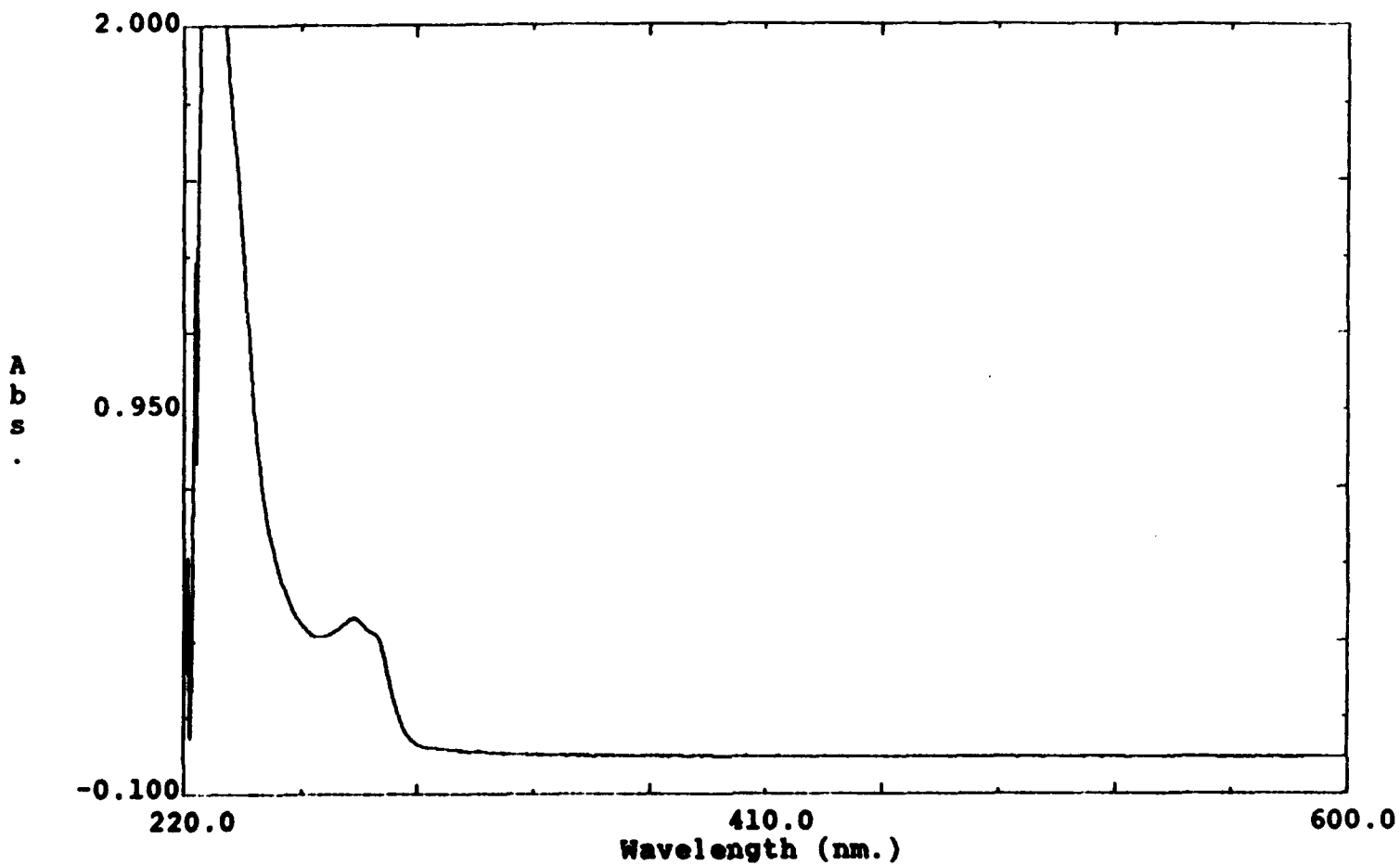
File Name: f4

No.	Peak Pick Wavelength (nm.)	Abs.
1	275.00	0.337
2	227.00	3.118

Created: 12:05 05/26/92
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Figure 12. Spectrum of the third batch of treated Freon.



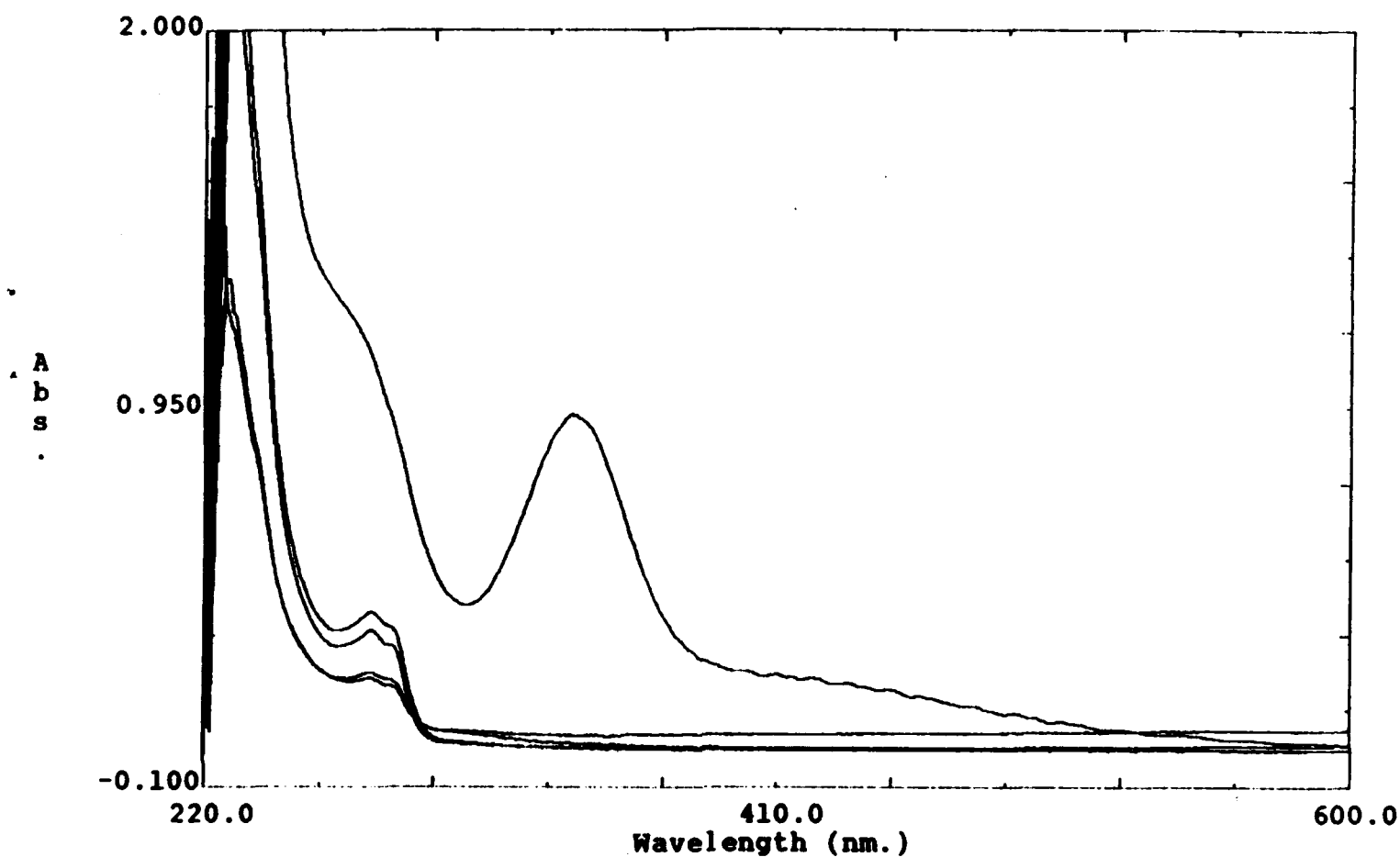
File Name: f5

Created: 12:09 05/26/92
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Peak Pick		
No.	Wavelength (nm.)	Abs.
1	531.50	0.003
2	388.00	0.005
3	348.50	0.009
4	275.00	0.387
5	226.00	5.000

Figure 13. Spectrum of the fourth batch of treated Freon.

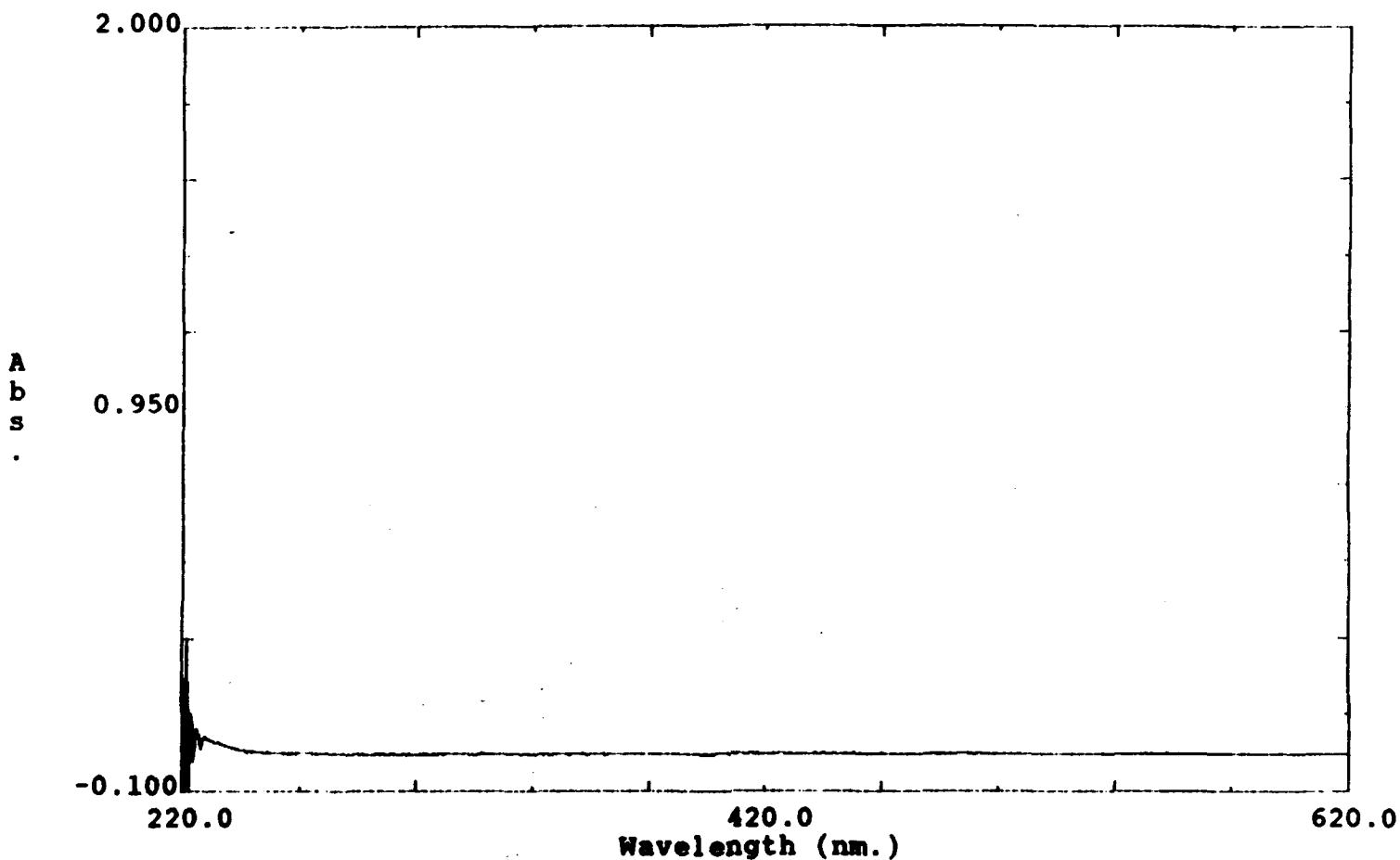


File Name: f2

Created: 10:56 05/26/92
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Figure 14. Combination of the previous five figures for comparison. The curves are identified from top to bottom at 275 nm as untreated Freon, fourth batch of treated Freon, third batch of treated Freon, second batch of treated Freon, and first batch of treated Freon.



File Name: f17

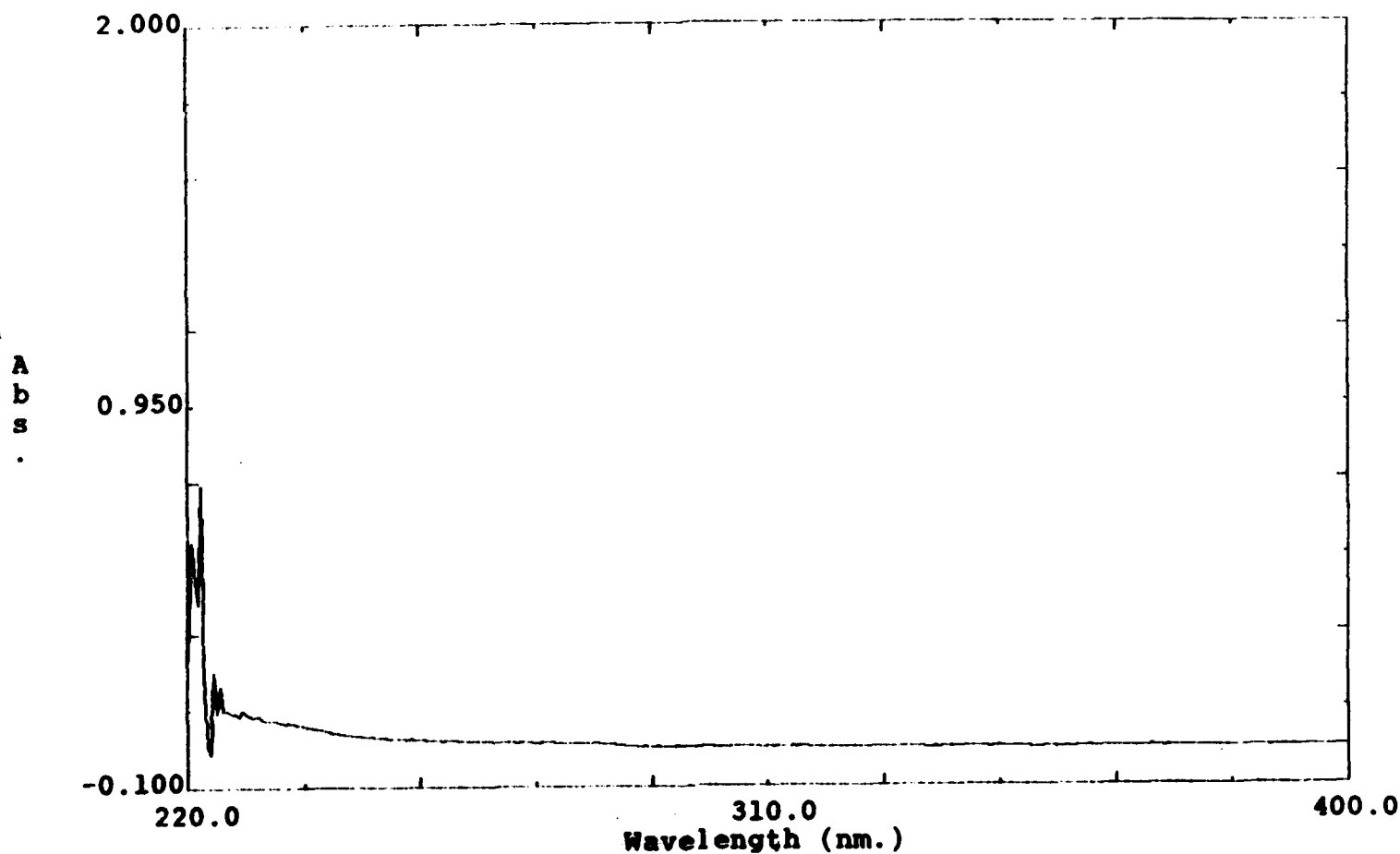
Freon/N₂O₄ contacted with
aqueous KOH for 15 minutes

Created: 10:01 08/05/92

Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Figure 15. Spectrum of Freon and N₂O₄
after extraction with aqueous KOH then 15
minutes of agitation. The N₂O₄ and Freon
solution was made up just before the
extraction.

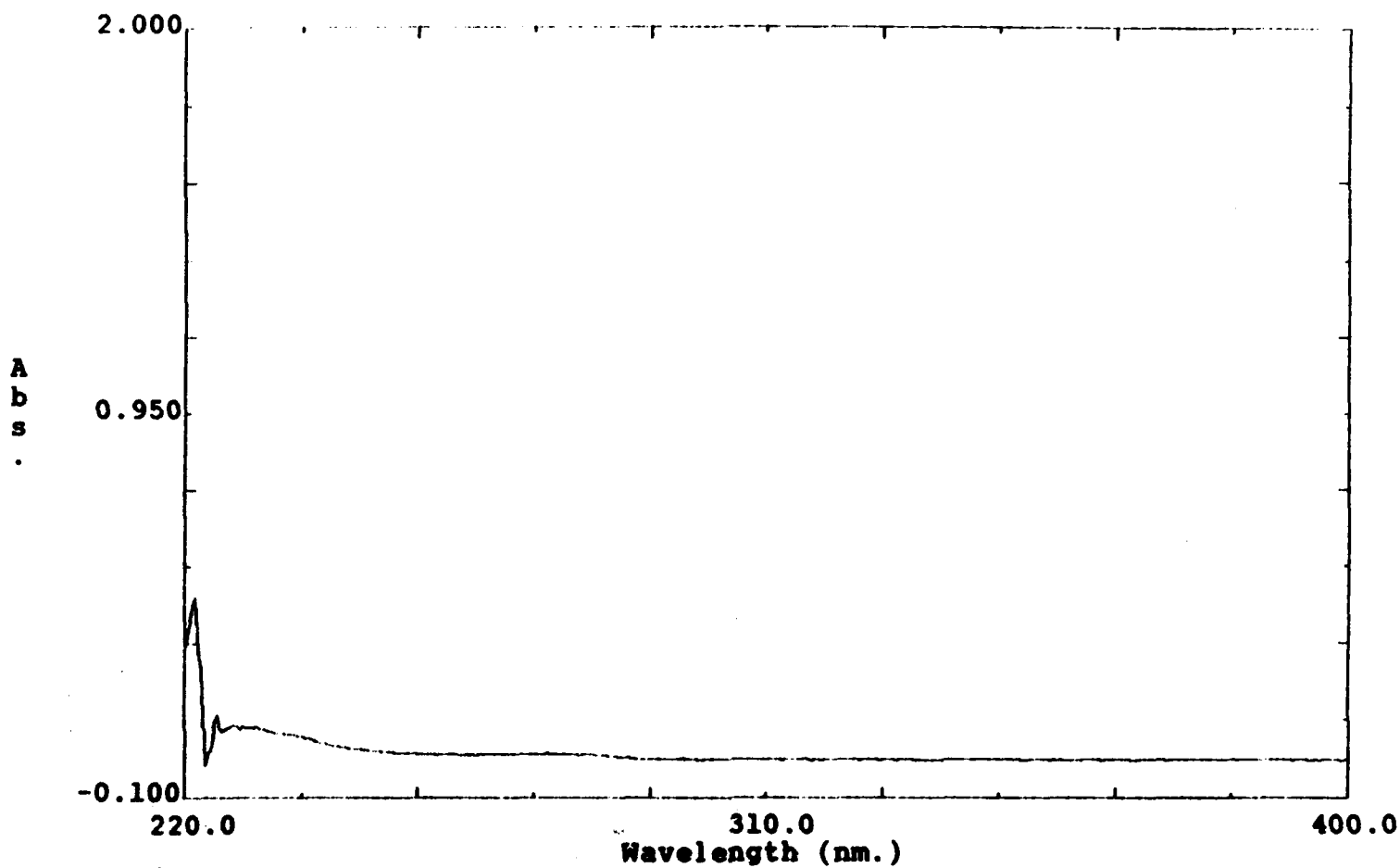


File Name: f9
freon contacted with NaNO3 aq

Created: 13:52 08/03/92
Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Figure 16. Spectrum of Freon after vigorous mixing with aqueous NaNO₃.



File Name: f11

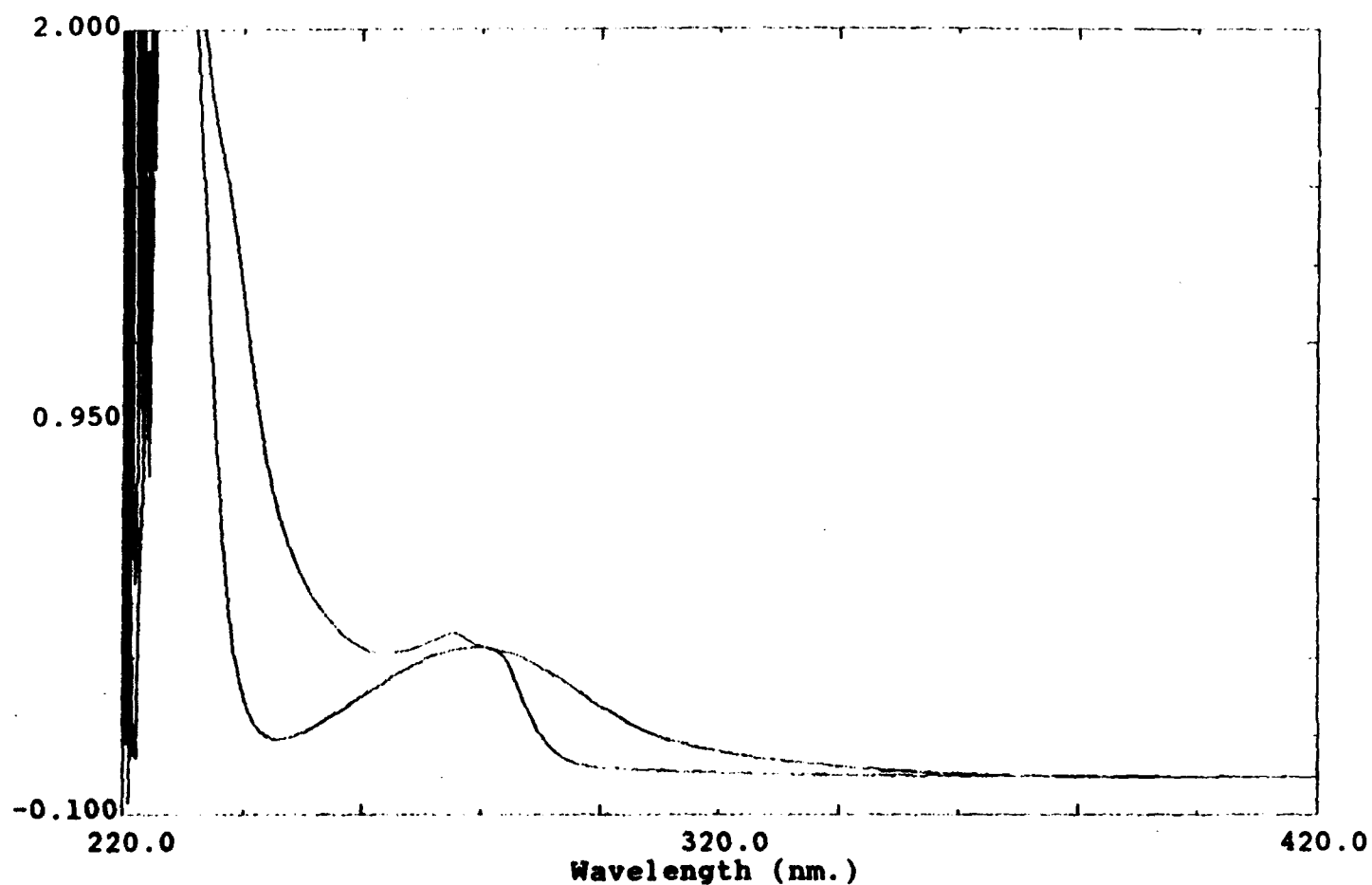
Freon contacted NaNO₂

Created: 14:33 08/03/92

Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.5

Figure 17. Spectrum of Freon after
vigorous mixing with aqueous NaNO₂.



File Name: f20

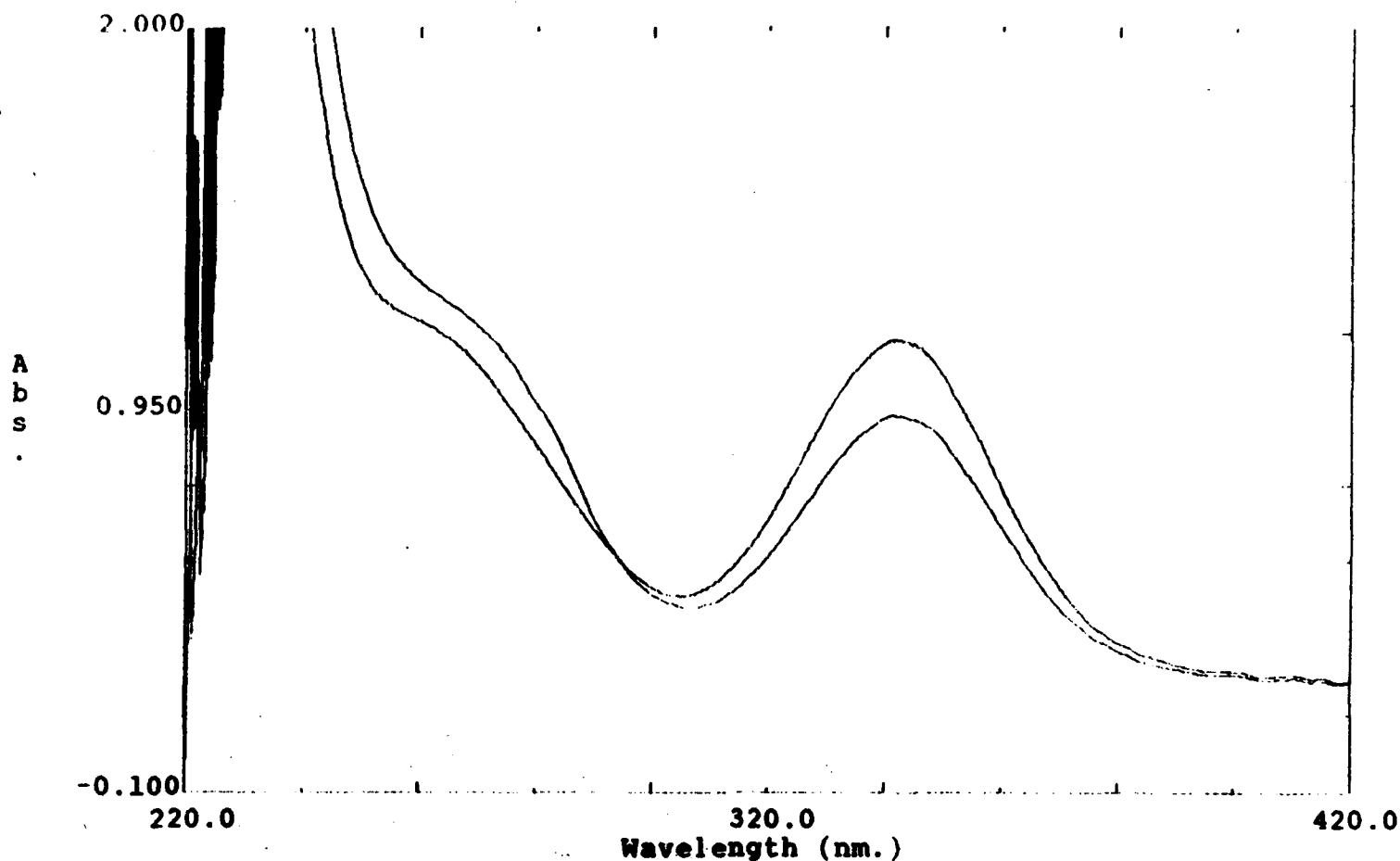
1-Nitropropane in Freon

Created: 10:08 08/07/92

Data: Original

Measuring Mode: Abs.
Scan Speed: Medium
Slit Width: 0.5
Sampling Interval: 0.2

Figure 18. Spectra of treated Freon and a solution of 1-nitropropane in Freon. At 300 nm, the top curve is the spectrum of 1-nitropropane in Freon, the lower curve is the spectrum of the third batch of treated Freon.



File Name: F23-2

MON 3 in Freon

Created: 09:26 08/10/92

Data: Original

Measuring Mode: Abs.
 Scan Speed: Medium
 Slit Width: 0.5
 Sampling Interval: 0.2

Figure 19. Comparison of old and new solutions of MON-3. At 340 nm the upper curve is the spectrum of the freshly made MON-3 in Freon solution, the lower spectrum is that of the contaminated Freon from WSMC. The curves are reversed at 260 nm.

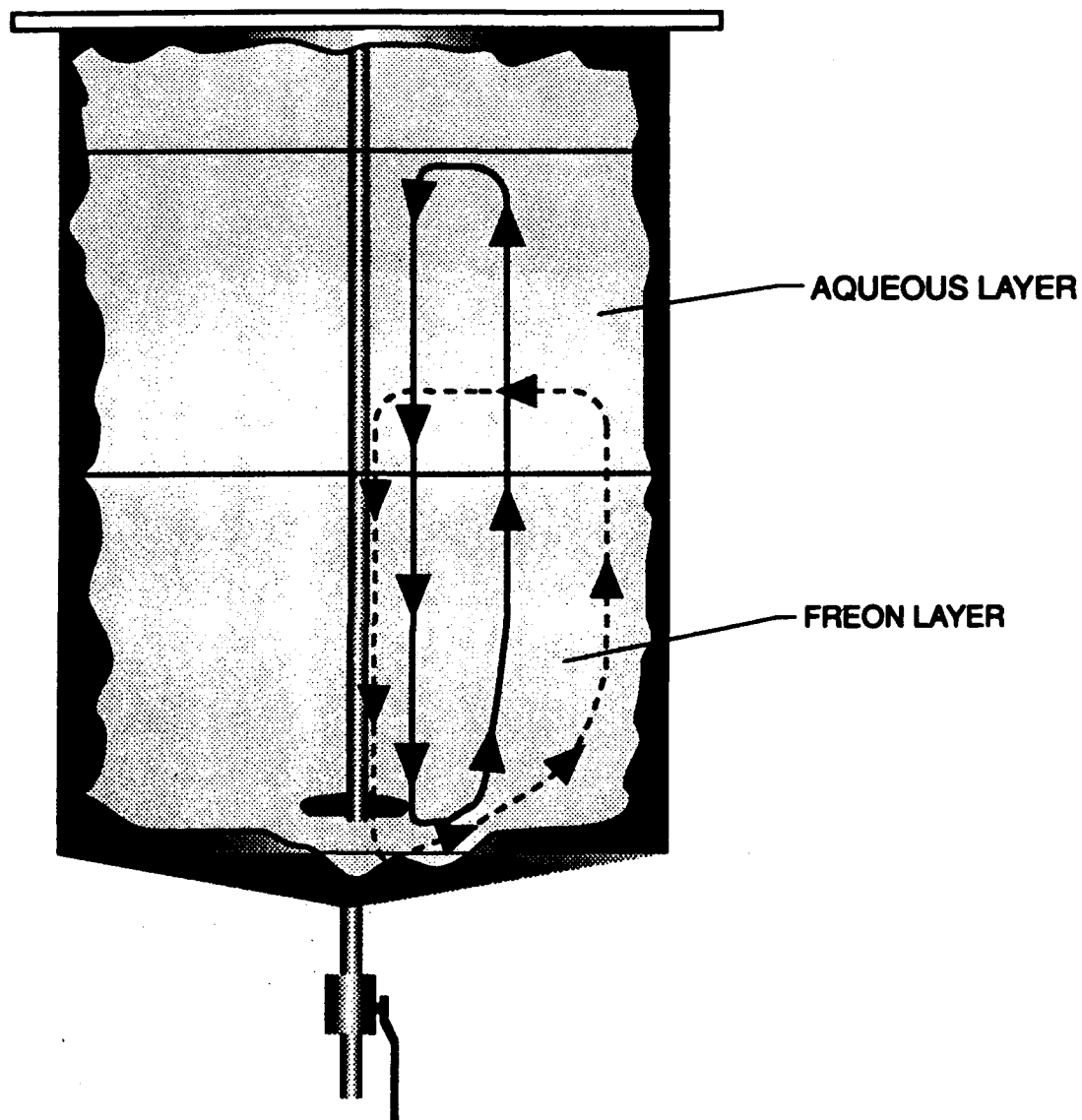


Figure 20 Cut Away View of Reactor Showing the Flow Pattern of the Two Phases. Solid Arrows are Water and Dashed Arrows are Freon.

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